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ABSTRACT

After a decade of slow but steady progress, the pace of development of technologies to deacidify and strengthen deteriorating books and documents has quickened significantly. These developments accentuate the need for the conservation community to scientifically evaluate the technical merits of potential processes. This draft evaluation strategy with accompanying protocols was prepared to help facilitate the development of meaningful criteria. The proposed model suggests that evaluations of any positive enhancements to the useful life of the paper be made first. These enhancements should be first, chemical in nature--i.e., measuring the extent of deacidification and buffering that the system provides. Second, the physical effects on paper properties and strengthening effects should be evaluated; these should be measured before and after accelerated aging of the test papers and their comparison with treated paper. Next, the physical strength of the aged treated and untreated materials should be compared to determine the extent of strengthening. These evaluations should be based on the chemical and physical requirements of the process as well as empirical evaluations of a range of treatable materials. If positive enhancement is found and no significant detrimental effects are seen, it is suggested that a review of safety and toxicology issues be made. In addition to detailed information on chemical and physical effects, this document includes materials on criteria for mass preservation, standard test materials, positive enhancement, accelerated aging, physical effects post accelerated aging, and non-detrimental effects. (SD)

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Evaluation Strategy Paper Preservation Systems February 12, 1990

Lithium Division

IR 053 361

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February 12, 1990

FMC

Re: Deacidification and Strengthening Process Evaluation Criteria

After a decade of slow but steady progress, the pace of development of technologies to deacidify and strengthen deteriorating books and documents has quickened significantly. These developments accentuate the need for the conservation community to evaluate scientifically the technical merits of potential processes. This is a worldwide issue. A number of individual libraries and institutions, as well as library groups, are grappling with the problem.

To help facilitate the development of meaningful criteria, we have developed a draft evaluation strategy with accompanying test protocols. This draft is not so much a recommendation as a "strawman" to help structure, focus and facilitate discussion by the conservation community.

There is little new work presented in our draft. We have tried to compile the best current thinking from around the world. We have not tried to identify the sources of the ideas or give credit to the individual contributors, since it has been difficult for us to tell where an idea originated. We hope that any lack of recognition here will be accepted in the spirit of helping move closer to mass preservation of the world's library collections.

To be complete, we believe, any evaluation plan must have the following components:

- Tests to be conducted (including the logic for the test and what it is designed to demonstrate)
- Well defined test protocol (reproducible by independent labs)
- Defined materials to be tested (available and reproducible)
- Defined satisfactory outcomes (either pass/fail criteria or at least, scales to quantify relative goodness or badness of test outcomes)

We have included these elements in our draft proposal.

We have left the evaluation of potential detrimental effects to empirical observation of treated materials. The range of materials is larger in the finished book. We have suggested areas of potential problems. These effects can potentially be quantified using the same elements for an evaluation plan suggested for the positive enhancements of paper life.

We have not included any proposals on toxicology evaluations. We have assumed that any potential supplier of services will have conducted sufficient relevant toxicology work to assure regulatory agencies and the public that no problems exist.

We would be pleased to discuss any aspect of this draft and the thinking behind the proposal. Please feel free to use any of the content without attribution to FMC.

Best regards.

FMC CORPORATION - LITHIUM DIVISION

Robert S. Wedinger

R. S. Wedinger, Ph.D.
Manager
Preservation Systems

TABLE OF CONTENTS

		PAGE
EVALUATION STRATEGY MODEL		5
SECTION I	CRITERIA FOR MASS PRESERVATION	9
SECTION II	STANDARD TEST MATERIALS	12
SECTION III	POSITIVE ENHANCEMENT	14
SECTION IV	CHEMICAL EFFECTS	19
SECTION V	PHYSICAL EFFECTS	44
SECTION VI	ACCELERATED AGING	82
SECTION VII	CHEMICAL EFFECTS POST ACCELERATED AGING	90
SECTION VIII	PHYSICAL EFFECTS POST ACCELERATED AGING	92
SECTION IX	NON-DETRIMENTAL EFFECTS	94

EVALUATION STRATEGY MODEL

EVALUATION STRATEGIES MODEL

PAPER PRESERVATION SYSTEMS

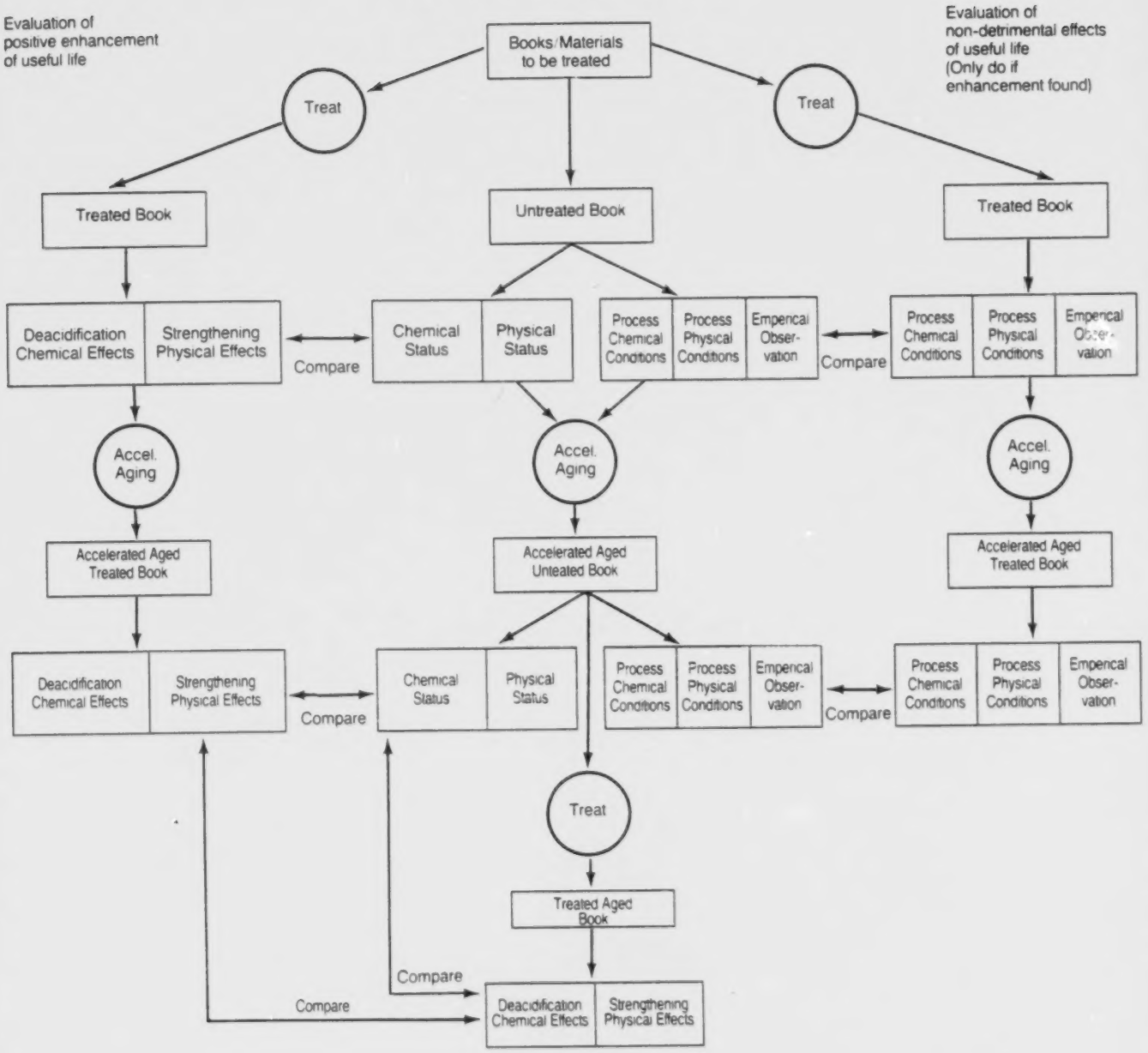
The following pages outline a strategy for the evaluation of alternative paper preservations systems. The model suggests that evaluations first be made of any positive enhancements to the useful life of paper. These enhancements should be first, chemical in nature; that is, measuring the extent of deacidification and buffering that the system provides. Second, the physical effects on paper properties, and strengthening effects, that the system imparts, should be evaluated. These should be measured before and after accelerated aging of the test papers and compared to untreated paper, both before and after accelerated aging. Finally the physical strength of aged treated and untreated materials are compared to determine the extent of strengthening

If the system provides positive enhancement to useful life, then the system should be evaluated for any potential detrimental effects.

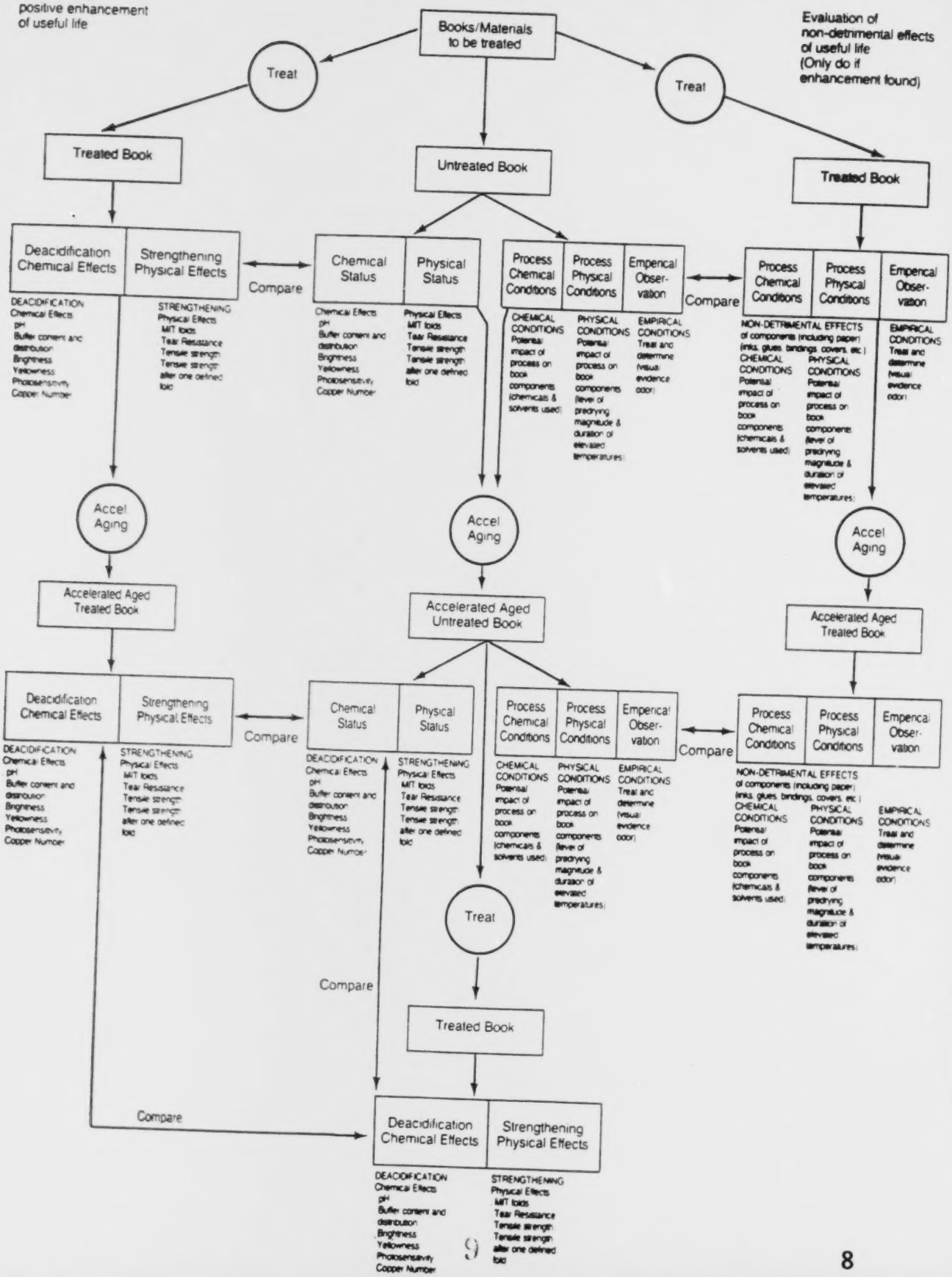
These evaluations should be made based on the chemical and physical requirements of the process as well as empirical evaluation of a range of treatable materials. To be most meaningful, these materials should be identified and standardized to the extent possible by the conservation community.

Finally, if positive enhancement is found, and no significant detrimental effects are seen, then a review of the safety and toxicology issues should be made.

Evaluation Strategy
Paper Preservation Systems



Evaluation Strategy
Paper Preservation Systems


Evaluation of positive enhancement of useful life
Books/Materials to be treated
Treat
Treated Book
Deacidification Chemical Effects
Strengthening Physical Effects
DEACIDIFICATION Chemical Effects pH Buffer content and distribution Brightness Yellowness Photosensitivity Copper Number
STRENGTHENING Physical Effects MIT folds Tear Resistance Tensile strength Tensile strength after one defined fold
Accel Aging
Accelerated Aged Treated Book
Deacidification Chemical Effects
Strengthening Physical Effects
DEACIDIFICATION Chemical Effects pH Buffer content and distribution Brightness Yellowness Photosensitivity Copper Number
STRENGTHENING Physical Effects MIT folds Tear Resistance Tensile strength Tensile strength after one defined fold
Compare
Untreated Book
Chemical Status
Physical Status
Chemical Effects pH Buffer content and distribution Brightness Yellowness Photosensitivity Copper Number
Physical Effects MIT folds Tear Resistance Tensile strength Tensile strength after one defined fold
Accel Aging
Accelerated Aged Untreated Book
Chemical Status
Physical Status
DEACIDIFICATION Chemical Effects pH Buffer content and distribution Brightness Yellowness Photosensitivity Copper Number
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Treat
Compare
Treated Book
Deacidification Chemical Effects
Strengthening Physical Effects
DEACIDIFICATION Chemical Effects pH Buffer content and distribution Brightness Yellowness Photosensitivity Copper Number
STRENGTHENING Physical Effects MIT folds Tear Resistance Tensile strength Tensile strength after one defined fold
Compare
Process Chemical Conditions
Process Physical Conditions
Emperical Obser-vation
CHEMICAL CONDITIONS Potential impact of process on book components (chemicals & solvents used)
PHYSICAL CONDITIONS Potential impact of process on book components (level of predrying magnitude & duration of elevated temperatures)
EMPIRICAL CONDITIONS Treat and determine (visual evidence odor)
Compare
Process Chemical Conditions
Process Physical Conditions
Emperical Obser-vation
CHEMICAL CONDITIONS Potential impact of process on book components (chemicals & solvents used)
PHYSICAL CONDITIONS Potential impact of process on book components (level of predrying magnitude & duration of elevated temperatures)
EMPIRICAL CONDITIONS Treat and determine (visual evidence odor)
Evaluation of non-detrimental effects of useful life (Only do if enhancement found)
Treat
Treated Book
Process Chemical Conditions
Process Physical Conditions
Emperical Obser-vation
NON-DETRIMENTAL EFFECTS of components (including paper) (inks, glues, bindings, covers, etc.)
CHEMICAL CONDITIONS Potential impact of process on book components (chemicals & solvents used)
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NON-DETRIMENTAL EFFECTS of components (including paper) (inks, glues, bindings, covers, etc.)
CHEMICAL CONDITIONS Potential impact of process on book components (chemicals & solvents used)
PHYSICAL CONDITIONS Potential impact of process on book components (level of predrying magnitude & duration of elevated temperatures)
EMPIRICAL CONDITIONS Treat and determine (visual evidence odor)

SECTION I

CRITERIA FOR MASS PRESERVATION

I. CRITERIA FOR MASS PRESERVATION

The deterioration of paper in books and archival material due to acid hydrolysis has been recognized since the turn of the century. Serious work on ways to mass deacidify and thus slow the deterioration of books began in the mid 1960s. Several processes have been developed to treat books, but all remain in various developmental stages.

The problem presently before conservators and preservation administrators is how to evaluate the results of the various mass deacidification processes in a comparable way to permit an informed decision on process selection. An additional task is to establish meaningful criteria and methods, as well as standards of measurement, such that developers and evaluators will have benchmarks from which to demonstrate process capability.

There are several methods for evaluating treated paper. The preferred methods are summarized in the following sections which are organized according to the model for evaluation strategy. No one or two tests are adequate for evaluating the effectiveness of paper treatment. Rather, results from all tests should be considered in an evaluation.

The following tests for the evaluation and comparison of treated and untreated papers are the ones which have been identified by conservators as having the most relevance for evaluating a process. The strategy as depicted in the model focuses the attention on identifying the positive enhancements imparted to a book during treatment. First the chemical characteristics are measured and compared to the same chemical characteristics of untreated material. The same hold true for the measurement and comparison of physical effects. The same physical and chemical characteristics are evaluated following accelerated aging. The measurement of the physical effects gives insight into the enhancement of projected life of the document due to aging.

A further evaluation to fully demonstrate strengthening characteristics of a process is conducted in two ways: 1) is to treat a naturally aged brittle book and measure the enhancement in physical characteristics post treatment. 2) take artificially aged paper and treat it, then measure the chemical and physical characteristics of it in comparison to the untreated samples.

Among the tests suggested as useful in following the degradation of paper with age, the folding endurance test is the most sensitive, giving significantly larger changes in value for a given aging period than the other tests.

For those not familiar with these tests, there are three important notes:

1. In carrying out these tests remember that paper is not a homogeneous material but differs in properties not only from sheet to sheet but from place to place within the sheet. It is important that multiple test samples be taken from any given batch of paper to obtain a reliable estimate of the mean value of any property. For most tests, 10 samples is a reasonable number.

2. Care should be taken to match the directional orientation of samples so that all are either in the machine direction or cross-machine direction due to the significant difference in values obtained from test results. In general, the machine direction values will be significantly higher with the exception of the Elmendorf tear test where the machine direction values are much lover.

3. Several references are made to significant differences. This means a confidence level of at least 95% as determined by statistical analysis.

SECTION II

STANDARD TEST MATERIALS

II. STANDARD TEST MATERIALS

Test papers should consist of the following three standards:

- Newsprint JCP - A10
- Alum-sized chemical pulp - bond paper - JCP-A60
- Alum-sized chemical pulp - 25% rag content - JCP - G40

The specifications for these papers are published by the U. S. Government Printing Office. This would allow companies to select similar papers if those recommended are not readily available.

It also should be pointed out that, when papers are purchased cut to size, the papers in a given box or ream may consist of papers from as many as five different batches of paper. This is because the sheeting cutters of paper suppliers are designed to cut papers from as many as five rolls of paper simultaneously, and there is no guarantee that all five rolls will come from the same batch of pulp or, for that matter, from the same mill. Where possible, paper for samples for testing should be taken from the same roll of paper. This can be assured if one obtains a stub roll of the desired paper from the paper supplier - that is, the end of a roll that has been used on the sheeting machine. This should be ample for any test series.

Samples of untreated paper should be retained and their chemical and physical characteristics should be measured as described in sections IV and V respectively. This then allows for comparisons to measure the positive enhancement of treatment. Similar books (e.g. from a series of encyclopedias) can likewise be retained in the untreated form to allow for empirical comparisons as described in Section IX.

SECTION III

POSITIVE ENHANCEMENT

III. POSITIVE ENHANCEMENT

The objective positive enhancements of treated paper are to be evaluated in accordance with the following two sections. It is important to note that to insure adequate comparisons the test strips should be treated similarly as follows:

All samples for physical tests are kept in a constant temperature and constant humidity (CT-CH) controlled room (70 ± 1°F and 50 ± 5% RH) for two weeks prior to testing (TAPPI T-402)*. Conditioning for two weeks is not always necessary, however, twenty four hours is ample time if the paper samples are hung so that air can circulate freely around each sample strip. What is important, if hysteresis effects are to be avoided, is that the samples be preconditioned in a drier atmosphere before placement in the CT-CH room so that each sample approaches equilibrium from the dry side; otherwise, the result could be samples having slightly different amounts of water at equilibrium, and this could affect the results.

Physical testing of the samples should be done in the CT-CH room. If the samples are removed for testing, the samples begin to change their water content very rapidly if there is a significant difference in the relative humidity and temperature in the testing room, thus the effect of the conditioning can be voided. Do not be misled by the time required to come to equilibrium. The change from one humidity level to another is exponential with time, and the approach to equilibrium is asymptotic so that the majority of the change can occur in the first few minutes.

The tests to be conducted are as follows:

CHEMICAL EVALUATION	PHYSICAL EVALUATION
.pH	.MIT Folds
.Buffer Content & Distribution	.Tear Resistance
.Brightness	.Tensile Analysis
.Yellowness	.Tensile Analysis after one defined fold
.Photosensitivity	
.Copper Number	

*TAPPI is the Technical Association of the pulp and paper industry which develops standardized testing procedures for laboratory analysis and process control for the paper industry. P.O. Box 105113, Atlanta Georgia 30348

T 402 om-88
OFFICIAL STANDARD – 1926
REVISED – 1970
OFFICIAL TEST METHOD – 1983
REVISED – 1988
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Standard conditioning and testing atmospheres for paper, board, pulp handsheets, and related products

1. Scope

1.1 This test method defines the standard atmospheres for normal preconditioning, conditioning, and testing of paper and paper products, paperboard, fiberboard, and containers made from them. It also specifies procedures for handling these materials in order that they may reach equilibrium with the respective atmosphere.

1.2 This test method is also applicable to standard pulp test handsheets, except that the preconditioning procedure is omitted, that is, the sheets are not dried to conditions below those obtained by exposure to the standard conditioning and testing atmospheres. (See T 205 "Forming Handsheets for Physical Tests of Pulp.")

1.3 This test method does not include special conditioning and testing atmospheres, such as those that attempt to simulate tropical or arctic environments.

2. Significance

2.1 The physical properties of a sample at 50% RH depend on whether the sample was brought to 50% from higher or lower relative humidities; this "humidity hysteresis effect" is 5-25% of the test value for many physical properties. For example, a hysteresis effect of 1.5% moisture content (or 25% of the test value of 6% moisture content) is typical. Preconditioning on the dry side within the range specified will avoid most of the hysteresis effect and result in the moisture content of a given sample being established within 0.15% when the sample is later conditioned to 50% RH and 23°C. Conditioning *down* to 50% gives most papers a moisture content very nearly the same as conditioning *up* to 60%.

2.2 Both temperature and relative humidity have significant effects on the physical properties of paper and board (*1*, 2.) For some properties of paper and board (e.g., MD tensile and CD stretch) a change of 1°C may have nearly as much effect as a change of 2% RH. For synthetic fibers and plastic laminates, the temperature effect may be greater than the RH effect.

3. Standard atmospheres

3.1 *Preconditioning atmosphere*, 10-35% RH and 22-40°C (72-104°F) (see Appendix).

3.2 *Conditioning atmosphere*, 50.0% ± 2.0% RH and 23.0 + 1.0°C (73.4 + 1.8°F.)

3.3 *Testing atmosphere*, same as for conditioning.

NOTE 1: It is important to distinguish between the overall limits of the temperatures within which conditioning and testing may be carried out and the limits within which the temperature must be maintained in order to maintain the specified relative humidity limits; i.e., the close temperature tolerance of ±1°C required in 3.2 and 3.3 will not in itself ensure the close relative humidity requirement of ±2% RH, as a sudden change of 1°C when at 23°C and 50% RH will change the RH about 3%.

4. Apparatus

4.1 *Preconditioning chamber*, a room or cabinet in which sample sheets or specimens may be individually exposed to circulating air at the preconditioning relative humidity and temperature.

Approved by the Physical Properties Committee of the Process and Product Quality Division
TAPPI

NOTE 2: For smaller sheets or specimens, the required preconditioning may be achieved easily with a simple cabinet, if no other means are available. If this cabinet is operated in a room maintained at 50% RH and 23°C and so designed that room air is drawn through it, and if the air entering and in the cabinet is heated to a temperature of 39 ± 1°C (102.2 ± 1.8°F), the relative humidity in the cabinet will be in the required range, i.e., 20% ± 3% RH. Commercially available forced-ventilation "ovens" should prove satisfactory. Input air to the oven should be drawn from the standard room, output should be vented outside of the standard room.

4.1.1 For many papers and boards, approximately the same preconditioning moisture content obtained by the above procedure may be achieved by using a sealed cabinet operated in a room maintained at 23 ± 1°C and using a saturated solution of lithium chloride (LiCl) to obtain a relative humidity of about 12-13%. For larger rooms needed for preconditioning sealed containers and large sheets, the required low relative humidity may be achieved by drawing air over a refrigerator expansion coil operating at a few degrees above freezing temperature.

4.2 *Conditioning and testing chamber*, one or more rooms or cabinets in which sample sheets or specimens may be individually exposed to circulating air at the conditioning relative humidity and temperature and then tested under the same conditions.

NOTE 3: The required relative humidity (50.0 ± 2.0%) and temperature (23.0 ± 1.0°C) are difficult to achieve, and therefore careful attention must be given to the design, evaluation, and maintenance of the "standard room." A separate procedure, TAPPI TIS 018-7, has been prepared for this.

4.3 *Hygrometer*, any instrument that can indicate directly or indirectly the relative humidity of the air with a calibrated accuracy of ±1.0% RH at 23°C and 50% RH.

4.4 *Thermometer*, either the dry bulb of a psychrometer (i.e., a hygrometer of the wet-and dry-bulb type) or a separate thermometer of any convenient design. If a separate thermometer, it should be graduated to 0.2°C (0.5°F) or closer with scale errors not exceeding these values. (Psychrometer thermometers must be graduated and correct to 0.05°C or closer and carefully matched to each other to give the required accuracy and repeatability in the measurement of relative humidity.) Wet-dry bulb psychrometry requires close attention to technique sources of error, purity of water, cleanliness of wick, proper air flow, and in particular the tightness of the wick on the temperature sensor.

5. Procedure

5.1 Obtain and preserve the sample in accordance with T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Product." In particular, avoid exposure of the sample to direct sunlight, to extremes of temperature, and to relative humidities above 58% (see Appendix A.1). If the sample is to be held for some time before testing, preserve it at a temperature below 25°C (77°F) and relative humidity below 58%, but not below 10% as the paper may curl or cockle and change in other respects.

NOTE 4: It has been reported that low temperature storage below 10°C (50°F) slows aging effects. Samples should be protected against condensation.

5.2 *Specimen preparation*

5.2.1 Cut specimens from a sample where critical dimensions are involved only after conditioning the sample. Where there are no critical dimensions, specimens may be cut before preconditioning or conditioning.

5.2.2 If shipping containers are to be sealed with aqueous adhesives, make the seal prior to preconditioning.

5.3 Expose the sample sheets or specimens to the preconditioning atmosphere so that both surfaces of single sheets and exterior surfaces of laminated products or sealed containers are freely exposed. This is best achieved by suspending them from overhead or supporting them on a wire grid or rack.

5.4 Precondition the sample sheets or specimens by exposing them as specified above (5.3) to the preconditioning atmosphere. Precondition for a minimum of 24 h, unless a lesser time has been found to give satisfactory results.

NOTE 5: For preconditioning apparatus of ample capacity and air circulation, the following preconditioning times have usually been found satisfactory: single sheets of paper, less than 1 h; liners, corrugating medium, chipboard, boxboard, 1-2 h; corrugated and solid fiberboard in sheet form, 5-10 h; sealed boxes and shipping containers, 12-16 h; specially treated water vapor resistant papers and boards, 24 h and more.

NOTE 6: If the sample is to be stored for some time after preconditioning, store at a temperature below 25°C (77°F) and a relative humidity below 40% but not below 10%.

5.5 Condition the sample sheets or specimens by exposing them as specified in 5.3 to the standard conditioning atmosphere for a sufficient time for them to come into equilibrium with the atmosphere. Determine that equilibrium has been obtained by weighing the sheets or specimens at time intervals which increase roughly geometrically. Plot the weight against log time (i.e., on semilogarithmic paper); the desired equilibrium exists when the plotted curve becomes essentially parallel to the time axis.

NOTE 7: With good air circulation and ample capacity, a conditioning period of 4 h is usually sufficient for paper of ordinary weight and composition. A minimum time of exposure of 5-8 h will be required for boards and unsealed boxes, with a minimum time of 16 h or more for sealed fiberboard boxes, and much longer periods for boards of heavy substances and specially treated water-vapor-resistant papers; e.g., a minimum of 72 h for wax-treated containers.

5.6 Handle preconditioned and conditioned sheets or specimens as little as possible; especially avoid touching or breathing on test areas.

5.7 Test the specimens in the standard testing atmosphere.

6. Report

6.1 Report the temperature, relative humidity, and total time of:

6.1.1 Preconditioning.

6.1.2 Conditioning before testing.

6.2 Report the minimum and maximum temperature and relative humidity during testing [1].

6.3 Report any variations in procedure from this method.

7. Additional information

7.1 Effective date of issue: June 1, 1988.

7.2 Related methods: ASTM D 685, ISO 187.

7.3 This method was corrected or revised in 1934, 1936, 1941, 1944, 1949, and 1970.

Appendix

Importance of preconditioning

A.1 For the sake of obtaining close interlaboratory agreement, especially on physical properties, a specified preconditioning procedure is necessary but not always sufficient. While preconditioning practically eliminates the hysteresis effect, it has little influence on strain relaxation effects. The latter depend on the entire previous moisture history of the sample, especially on the conditions of initial drying and tension, and on the duration and degrees of subsequent excursions to high humidities (i.e., above about 58% RH). Consequently, for very close interlaboratory agreement a procedure for handling the sample from manufacture to testing is required.

A.2 For mill control and similar within-one-laboratory purposes, the preconditioning step may often be eliminated. For some properties and materials, preconditioning may not be necessary, either because of the smallness of the humidity hysteresis effect or because of lower test accuracy requirements.

References

1. Wink, W. A., *Tappi* **41** (6): 171A (1961.)
2. Crook, D. M., and Bennett, W. E., *Brit. Paper & Board Industry Research Association*, Report RA/T/90, Feb. 1962.

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Test Methods Administrator. ■

[1] Report moisture content of material at time of test in order to reproduce test results. This is especially important for corrugated and solid fiberboard and containers.

SECTION IV

CHEMICAL EFFECTS

IV. CHEMICAL EFFECTS

Deacidification is performed to enhance the lifetime of treated materials. Hence, the resulting pH should be on the alkaline side and an adequate amount of buffer should be left to retard reacidification. It is important to obtain a consensus on methods for the technical assessment of alternative deacidification process.

The following are recommended procedures to be employed to evaluate the desired changes.

A. Hydrogen ion Concentration (pH)

An alkaline pH is required for maximum permanence. The glucosidic bonds of the polysaccharides are stable in neutral and moderately alkaline environments. The Society of American Archivals requires a minimum pH of 8.0 for permanent paper. There is some justification for setting a maximum pH, as papers with very high alkalinity (pH 11.0 or greater) are subject to increase the possibility of alkaline hydrolysis. Although the Library of Congress has reported no adverse effects in evaluating paper properties at a pH of 10.3.

Two methods for the determination of pH have been standardized. These are the hot extraction method, TAPPI T-435, and the cold extraction method, TAPPI T-509. The cold water extract is obtained by soaking the sample in distilled water for one hour, and the hot water extract is secured by boiling the sample in distilled water for the same length of time. Either method is acceptable, although they can yield different results. In the hot method, acid or alkaline salts are hydrolyzed resulting in either more acidic or more alkaline results depending upon the salts present. The cold extraction is generally preferred.

The hydrogen ion concentration of an aqueous extract is therefore to be determined according to TAPPI Method T-509. The Library of Congress has found that the time required for a reliable pH reading can be shortened to approximately five minutes by reducing the sample to pulp in a miniature Waring blender, as opposed to allowing the macerated paper to soak for one hour. The modified method has been demonstrated to agree with the standard method and saves considerable time. Two grams of paper are homogenized in 200 ml of CO_2 free, distilled water. The pH of the slurry is then measured. **The pH of the treated paper shall not be less than 7.0 and not greater than 10.5 as measured by the TAPPI cold extraction method.**

B. Residual Buffer Content and Distribution

Hot water extractable alkalinity of paper can be measured by TAPPI Method T-428. There is also an ANSI-ASTM procedure for determining calcium or magnesium carbonate quantities in paper. One titrates one gram (weighed to nearest 0.001 gram) of paper on a dry basis in 25 ml

of water in a 125 ml Erlenmeyer flask. Twenty ml of 0.1N hydrochloric acid is pipetted into the flask, and the mixture is boiled briefly to expel carbon dioxide. Three drops of methyl red indicator are added; the solution is cooled to room temperature and titrated with standardized 0.1N sodium hydroxide solution to a lemon yellow endpoint. The results are calculated as percent calcium carbonate with the following equation:

$$CaCO_3\ \% = \frac{(ml \times N)_{HCl} - (ml \times N)_{NaOH} \times 0.050 \times 100}{\text{Weight of Specimen, g}}$$

The titration can also be made with a pH meter. The endpoint of the methyl red indicator is at pH 5.8. It may be preferable to use a pH meter in the titration of paper acidity or alkalinity, particularly with aged papers which can contribute considerable color to the solution making the methyl red endpoint difficult or impossible to judge.

One can also use pH 7 as the endpoint of the titration. If the acid and alkali solutions are standardized to the pH 7 endpoint, there is no difference in the result. In any case, there is never more than one or two drops of difference in the titration with methyl red and a pH meter pH 7 endpoint. With relatively inexperienced personnel the titration is much easier with the pH meter and much more reproducible as the methyl red indicator is very much dependent upon the background and lighting for reproducible results.

In addition to TAPPI Method T-428, and the ANSI-ASTM procedure for determining magnesium carbonate filler in paper, the alkalinity of the paper can also be measured in the same slurry used for the determination of pH (200 ml of water). The sample is titrated to a pH of 4.8 using a pH meter. The titration is done with 0.25N HCl if the initial slurry pH is above 8.0 and with 0.1N HCl if the initial slurry pH is below 8.0. The results are calculated as percent magnesium carbonate equivalent using the following equation.

$$MgCO_3\% = \frac{\text{ml acid} \times \text{N acid} \times 4.2165}{\text{sample weight, (grams)}}$$

The amount of buffer should be reported as percent $MgCO_3$ equivalent and should be evaluated over the entire page and book to determine the uniformity of distribution. This can be accomplished by dividing the page into six equal sections and measuring the buffer content of each according to the prescribed procedure. **The buffer reserve of treated paper shall not be less than 0.5% $MgCO_3$ equivalent. For a given paper type, the relative standard deviation shall not be greater than 15% in either direction.**

C. Brightness/Yellowness

TAPPI Method T-452 describes the procedure for the determination of the brightness of paper. Brightness instability is indicative of decomposition products which also contribute to the deterioration of paper. The brightness of paper usually decreases during aging. A reflectometer is used to simultaneously measure the relative yellowness and brightness of treated versus untreated paper. The degree of yellowing is related to the presence of oxidized functionalities, as the number of carbonyl groups increases, so does the per cent of yellowness. This is therefore, related to the copper number. Of course paper with a high lignin content generally "yellows" upon deacidification due to an increase in the aromaticity properties of the lignin structure. The comparison standards are barium sulfate for brightness and ferric sulfate for yellowness. Results are reported as percent versus the standard.

The measurements are done over six paper thicknesses to avoid background errors. (If it is impossible to provide six thicknesses, the measurement can be done over the standard barium sulfate plate as the background for comparison, provided the other samples are also measured over the same barium sulfate plate.)

The percent reflectance differences between treated and untreated paper shall not be more than +5% with regard to brightness. The yellowness values are reported and compared to untreated material. **The differences in yellowness between the averages of non-lignin containing paper shall not be more than 15%.**

D. Photosensitivity

Photochemical degradation is in general of less importance for books which are stored in a library in general darkness however, photosensitized oxidation can be an important degradative process. The effect of light on the mechanical properties of paper has not been exhaustively studied. The direct photolysis of cellulose requires wavelengths in the ultra-violet region (<300 nm). These wavelengths are not commonly found in either daylight or ordinary light sources and therefore this mode of degradation is of no concern. Photosensitized decomposition of cellulose is, on the other hand, something which can take place at the wavelengths present in normal light sources. The cellulose itself does not absorb this radiation, it must be absorbed by sensitizers such as Fe^{+3} which initiate photochemical reactions.

A comparison of photo-chemical sensitivity differences between treated and untreated paper is suggested by the Library of Congress, to insure that the salts deposited as a buffer reserve do not act as photosensitizers and thus lead to this mode of degradation. Their recommended procedure is to expose the papers for twelve days to UV irradiation at an intensity level of 2500-3500 $\mu W/cm^2$ in the wavelength range 250-400 nm and a percent RH range of 40-60%. The paper degradation behavior is to be evaluated by the MIT fold endurance test. **The treated paper shall have an average value which is not significantly lower than untreated paper following this exposure.**

E. Copper Number

It has been well established that hydrolyzed and subsequently oxidized cellulose is capable of reducing various metallic ions to lower valence states. Reactions of this type have served to detect damage to cellulose and to estimate the quantity of carbonyl groups. It is generally used for determining changes accompanying deterioration and is therefore considered as a factor having an indirect bearing on the permanence of paper.

The copper number is defined as the grams of metallic copper (as Cu_2O) resulting from the reduction of cupric sulfate ($Cu\ SO_4$) by 100g of the pulp or paper fibers. The test is conducted as described in TAPPI Test 430. This test is to be performed on treated and untreated, aged paper. The values obtained are indicative of the amount of oxidized moieties. **Treated paper should have average values significantly less than the average value of untreated paper.**

CAUTION:
This method may require the use of some chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Material Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this test method, the user should determine whether any of the chemicals to be used are potentially hazardous and, if so, should follow strictly the procedures specified by both the manufacturer, as well as state and federal authorities, for safe use of these chemicals.

T 509 om-88
SUGGESTED METHOD – 1968
OFFICIAL STANDARD – 1977
OFFICIAL TEST METHOD – 1983
REVISED – 1988
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Hydrogen ion concentration (pH) of paper extracts (cold extraction method)

1. Scope

1.1 This method measures the hydrogen ion concentration of a cold aqueous extract (unfiltered) of paper, expressed in terms of pH value.

1.2 It is suitable for writing, printing, and sized industrial papers, but is not intended for unbuffered types such as insulating and condenser papers. The determined values may not be exact in a fundamental sense and should not be interpreted in terms of solution theory. The pH values are empirically correlated with end use requirements and paper qualities. This method avoids change of acidity or alkalinity resulting from heat-induced hydrolysis.

1.3 A hot water extraction method is described in TAPPI T 435, "Hydrogen Ion Concentration (pH) of Paper Extracts (Hot Extraction Method)."

2. Summary

This method consists of a cold water (25 ± 5°C) extraction of the specimen for one hour followed by a pH measurement with a commercial pH meter.

3. Significance

The pH determination measures the extent to which the paper alters the hydrogen-hydroxyl equilibrium of pure water. The pH (acidity) is important because of its effect on the permanence of the paper. Although the acidity may be determined as the amount of water soluble acidity by titration with alkali, the hydrogen ion concentration (pH) is more indicative of the stability of paper than is the total acidity.

4. Definitions

4.1 *pH*, the negative logarithm (to base 10) of the hydrogen ion concentration of a solution.

4.2 *Paper acidity*, the extent to which water-soluble materials in the paper alter the hydrogen-hydroxyl equilibrium of pure water causing an excess of hydrogen ions as measured by a commercial pH meter under specified conditions.

4.3 *Paper alkalinity*, the extent to which water-soluble materials in the paper alter the hydrogen-hydroxyl equilibrium of pure water causing an excess of hydrogen ions as measured by a commercial pH meter under specified conditions.

5. Apparatus

5.1 *pH meter*, a commercial pH meter including a glass electrode, reference electrode, and electronic circuitry that will measure emf and indicate pH directly with a precision of 0.1 pH unit. The circuit should include temperature compensation.

5.2 *Other apparatus:* 100- and 300-mL beakers and watch glasses; 100- and 1000-mL graduated cylinders; glass stirring rod.

6. Reagents

6.1 Distilled water. (Deionized water, if used, must be checked each time water is drawn for pH tests.)

6.1.1 The water may contain CO_2 in equilibrium with the atmosphere, but no other acidic material. The pH should not be less than 5.9. Test for presence of alkaline impurities by boiling two specimens of approximately 100 mL each for 15 minutes. Cover each with a watch glass and cool to room temperature. Wash the electrodes well with distilled water, then with the boiled water. Measure the pH of both specimens. If these are not between 6.2 and 7.3, redistill the water as described in the Appendix. The redistilled water must meet the above requirements.

6.1.2 For referee tests, check the water as follows: Heat 100 to 125 mL of the distilled water to boiling, but do not continue boiling. While the water is cooling and being

checked (for pH and conductivity) pass prepurified nitrogen or CO_2-free air through it, using a 90°-angle type gas dispersion tube with 20 or 30 mm coarse fritted disk. Air, if used, should be oil-free. Pass the air through a gas washing bottle containing at least 200 mL of 1.5*M* H_2SO_4 and then through a tower or U-tube containing ascarite or soda lime, 120 to 150 mm long, before connecting the air to the gas dispersion tube. There should be a slow but steady flow of small bubbles. When the water has cooled to room temperature, insert the pH electrodes, continuing the nitrogen or airflow until the pH meter indicates equilibrium, but discontinue the flow while taking the final reading. When tested by this method, the water must have a pH between 6.8 and 7.3.

6.1.3 The conductivity of water used for referee testing should not exceed 1.5 µS/cm after the above treatment (1).

6.2 *Standard buffer solutions.*

6.2.1 *Potassium hydrogen phthalate buffer*, pH 4.01 at 25°C. Dissolve 10.21 grams of $KHC_8H_4O_4$ (ACS primary standard or certified grade) in water and dilute to 1000 mL.

NOTE 1: As the buffer capacity of this solution is rather low, protect the solution from contamination with acids and alkalies. However, the pH is not affected by atmospheric carbon dioxide. The solution should be replaced after six weeks, or earlier if mold appears.

6.2.2 *Phosphate buffer*, pH 6.86 at 25°C. Dissolve 3.40 grams of monobasic potassium phosphate KH_2PO_4 (ACS Primary standard) and 3.55 grams anhydrous dibasic sodium phosphate, Na_2HPO_4, in carbon dioxide-free water and dilute to 1000 mL.

NOTE 2: The Na_2HPO_4 will absorb moisture at relative humidities exceeding about 40% at 25°C and should be dried for two hours at 110 to 130°C before use. This buffer solution is quite stable when protected from undue exposure to the atmosphere.

6.2.3 *Potassium hydrogen tartrate buffer*, pH 3.56 at 25°C saturated solution. Add 1 g of $KHC_4H_4O_6$ to 100 mL water at about 30°C, shake for several minutes, cool to 25°C, decant, and filter.

NOTE 3: The pH is insensitive to changes of concentration and elaborate precautions to ensure saturation are unnecessary. The temperature of saturation may vary from 22 to 28°C. Excess solid should be removed as it may cause erratic potentials at the liquid junctions. The tartrate solution is subject to molding accompanied by an increase in pH. Consequently, it cannot be used for more than a few days unless a preservative, such as a crystal of thymol, is added.

6.2.4 *Borax buffer*, pH 9.18 at 25°C: Dissolve 3.81 g (air weight) of $Na_2B_4O_7{\cdot}10H_2O$ in carbon dioxide-free water and dilute to 1000 mL.

NOTE 4: The dilution value of this solution is so small that changes in the water content of the borax are usually of no concern. Precautions should be taken to protect the solution from exposure to atmospheric carbon dioxide. It is advisable to replace the solution about a month after preparation.

6.2.5 *Proprietary buffers.* These are permitted provided they are of the proper pH value.

7. Calibration

Before measuring the pH of the specimen solution, calibrate the pH meter at pH 4.01 using the phthalate buffer, and check the phosphate buffer, which should have a pH of 6.80-6.90. When more than five tests are made, the pH meter should be recalibrated after the first five tests and between each subsequent series of five tests using the buffer having a pH nearest the test solution. The pH meter should *always* be recalibrated when it has not been used for an hour or more.

8. Sampling

Obtain a sample of the paper in accordance with TAPPI T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Product."

9. Test specimen

9.1 A composite evaluation is considered appropriate for this test unless otherwise specified.

9.2 Take an equal number of sheets (one or more) from each test unit, but not less than a total of five sheets, and combine the sheets from all test units. Holding the sheets at one end, cut and cross-cut the other end into 5-10 mm squares. Do not include any papers touched with the fingers. From each quantity of cut paper, weight a test specimen of 1 ± 0.01 g.

9.3 Perform determinations at least in duplicate. In special cases where it is necessary to evaluate different portions of the lot separately, take a portion from each test unit of the sample and perform duplicate determinations on each portion independently, using the procedure specified for the composite.

10. Procedure

10.1 Transfer the test specimen to a 100-mL beaker. Add about 5 mL of distilled water and macerate with a flattened glass stirring rod until the specimen is wet.

10.2 Add more water to bring the volume to 70 mL, stir well, cover with a watch glass, and allow to stand for one hour at room temperature (25 ± 5°C). The specimen may stand for three or four hours (2) if no contamination occurs.

10.3 When making referee or research tests, pass pure nitrogen or CO_2-free air through the solution during cooling and until measuring pH as directed for checking water, but omit the heating.

NOTE 5: Air may be cleaned by passing it through a gas washing bottle containing at least 200 mL of 3*N* H_2SO_4 and then through a tower or U-tube containing ascarite or soda lime, 120-150 mm long.

10.4 After calibrating the instrument, stir and measure to 0.1 pH unit the pH of the extracted unfiltered mixture according to the instructions for the type pH meter used. Keep the electrodes, buffer, test solution, and wash water at the same temperature and be sure the compensator is set for this temperature. Before recording the pH leave the electrodes in the solution until there is no measurable drift in 30 s.

10.5 Wash the electrodes with distilled water after each measurement and recalibrate frequently.

10.6 Do not wash glassware with soap or detergent; use an acid cleaning solution and rinse adequately.

11. Report

Report the average of two determinations to the nearest 0.1 pH unit.

12. Precision

12.1 Repeatability (within a laboratory) = 2.1% for comparison of test results from the same test unit, where each test result is the average of two determinations, one each on separate sheets from the same test unit. Repeatability on test results from the same composite sample, as specified in this method, should be equal to or smaller than this figure.

12.2 Reproducibility (between laboratories) = 10.4%. The above is the average calculated from data taken from 14 reports on the Collaborative Reference program for paper.

12.3 Comparability = not known.

13. Additional information

13.1 Effective date of issue: March 16, 1988.

13.2 The pH value of a cold water extract is usually different from that of a hot extract. The pH of a hot extract of paper sized with rosin and alum is typically 0.5 or 0.6 unit lower than that of a cold extract. This difference is due to hydrolysis of the alum or basic sulfates retained in the paper (*3*). Proponents of the hot extraction believe that the hydrolysis simulates changes which might occur during natural aging (*4,5*). Barrow (*2*), however, found that cold extraction correlated better with his accelerated aging tests.

13.3 It has been found (*6*) that melamine-formaldehyde resin hydrolyzes during hot extraction and releases alkaline products which tend to increase the pH value of the extract. Consequently, when a paper contains both alum and melamine resin, the pH of the hot extract may be higher, or lower than, or equal to the cold extract value. Other materials are believed to have a similar effect. Thus a value obtained after hot extraction might be misleading.

13.4 Other methods of measuring paper pH have been proposed: In the French Standard Method (*7*), the paper is extracted with neutral solutions of KCl. This is further discussed by Palenius et al. (*8*). The pH of a solution on the surface may be measured with surface electrodes (*8-11*). An extrapolation procedure for textiles has also been investigated (*12-14*). Another method is to make spot tests with indicator solutions (*15*).

13.5 Related methods: French AFNOR NFQ 03-005; British Standard 2924; Scandinavian Standard SCAN-P14; and Canada CPPA G.25; Australian APPITA P 421.

13.6 An additional list of references is given in *Tappi* **50** (12): 189A(1967).

Appendix

Treatment of distilled water

A.1 Usually, simple distilled water is satisfactory for use in this method, but the quality of water required is a very important factor. It was found (*8*) that the difference between two lots of water caused a difference of 0.5 pH units in the extract. Water which does not meet the requirements given in Section 6 should be redistilled.

A.2 Entrained material can usually be removed by distilling with a high-capacity glass still. When distilling from solutions with added chemicals to avoid volatile contaminants, great care must be taken to avoid entrainment. Stills with double heads or traps should be used. Anti-bump material should be added and the distilling rate reduced.

A.3 To remove acid or organic material, distill the water from a solution containing 1 g of $KMnO_4$ and 4 g of NaOH per liter (*16*). This does not remove ammonia, so any volatile alkalinity is best removed by distilling from very dilute sulfuric acid (*16*).

14. References

1. ASTM Standard D-1193.
2. Barrow, W. J., *Tappi* **45**: 468 (1962).
3. Reynolds, W. F. and Linke, W. F., *Tappi* **46**: 410 (1963).
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14. Reif, J., *Deut. Textiltech.* **12**: 434 (1962); *Chem. Abstracts* **58**: 609.
15. TAPPI Useful Method 441: TAPPI Useful Method 471.
16. Taylor, J. E., *J. Chem. Educ.* **37**: 204 (1960).

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Test Methods Administrator. ■

CAUTION:
This method may require the use of some chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Material Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this test method, the user should determine whether any of the chemicals to be used are potentially hazardous and, if so, should follow strictly the procedures specified by both the manufacturer, as well as state and federal authorities, for safe use of these chemicals.

T 435 om-88
TENTATIVE STANDARD – 1934
SUGGESTED METHOD – 1968
OFFICIAL STANDARD – 1977
OFFICIAL TEST METHOD – 1983
REVISED – 1988
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Hydrogen ion concentration (pH) of paper extracts (hot extraction method)

1. Scope

1.1 This method measures the hydrogen ion concentration, expressed in terms of pH, of an aqueous extract of paper obtained by hot extraction (unfiltered and extracted by boiling water for one hour).

1.2 It may be applied to writing, printing and sized industrial paper, but it is not intended for unbuffered types such as electrical insulating and condenser papers. Values determined by this method will reflect changes resulting from heat-induced hydrolysis.

1.3 The cold extraction method is now described in T 509.

2. Summary

This method consists of a boiling water extraction of the specimen for one hour followed by a pH measurement with a commercial pH meter.

3. Significance

The pH determination measures the extent to which the paper alters the hydrogen-hydroxyl equilibrium of pure water. The pH (acidity) is important because of its effect on the permanence of the paper. Although the acidity may be determined as the amount of water soluble acidity by titration with alkali, the hydrogen ion concentration (pH) is more indicative of the stability of paper than is the total acidity.

4. Definitions

4.1 pH, the negative logarithm (to base 10) of the hydrogen ion concentration of a solution.

4.2 *Paper acidity*, the extent to which water soluble materials in the paper alter the hydrogen-hydroxyl equilibrium of pure water causing an excess of hydrogen ions, as measured by a commercial pH meter under specified conditions.

5. Apparatus

5.1 *pH meter*, A commercial pH meter including a glass electrode, a calomel reference electrode, and a potentiometer that will measure emf and indicate pH directly with a precision of 0.1 pH unit. The circuit should be compensated for temperature.

5.2 *Erlenmeyer flasks*, 125-mL with standard taper joint.

5.3 *Reflux condensers*, preferably water cooled, West or Allihn Type, with 300 mm jackets, standard taper inner joints and drip tips; or *air condensers*, 10-mm diameter and 1000 mm long with ST inner joints and drip tips, ST joints to fit the flasks.

5.4 *Other apparatus*: 100-mL beakers; 100 ml graduated cylinder; stirring rods, all carefully cleaned and rinsed with distilled water before use.

6. Reagents

6.1 *Distilled water*. (Deionized water, if used, must be checked each time water is drawn for pH tests.)

6.1.1 The water may contain CO_2 in equilibrium with the atmosphere, but no other acidic material. The pH should not be less than 5.9. Test for the presence of alkaline impurities by boiling two specimens of approximately 100 mL each for 15 minutes. Cover each with a watch glass and cool to room temperature. Wash the electrodes well with water, then with the boiled water. Measure the pH of both specimens. If these are not between 6.2 and 7.3, redistill the water as described in the Appendix. The redistilled water must meet the above requirements.

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TAPPI

6.1.2 For reference tests, check the water as follows: Heat 100-125 mL of the distilled water to boiling, but do not continue boiling. While the water is cooling and being checked (for pH and conductivity) pass prepurified nitrogen or CO_2-free air through it, using a 90°-angle type gas dispersion tube with 20- or 30-mm coarse fritted disk. Air, if used, should be oil-free. Pass the air through a gas washing bottle containing at least 200 mL of approximately 1.5 M and then through a tower or U-tube containing ascarite or soda lime, 120-150 mm long, before connecting the air to the gas dispersion tube. There should be a slow but steady flow of small bubbles. When the water has cooled to room temperature, insert the pH electrodes, continuing the nitrogen or air flow until the pH meter indicates equilibrium, but discontinue the flow while taking the final reading. When tested by this method, the water must have a pH between 6.8 and 7.3.

6.1.3 The conductivity of water used for referee testing should not exceed 1.5 µS/cm after the above treatment.

6.2 *Standard buffer solutions*:

6.2.1 *Potassium hydrogren phthalate buffer*, pH 4.01 at 25°C. Dissolve 10.21 grams of $KHC_8H_4O_4$ (A.C.S. Primary Standard or certified grade) in water and dilute to 1000 mL.

NOTE 1: As the buffer capacity of this solution is rather low, protect the solution from contamination with acids and alkalies. However, the pH is not affected by atmospheric carbon dioxide. The solution should be replaced after six weeks, or earlier if mold appears.

6.2.2 *Phosphate buffer*, pH 6.86 at 25°C: Dissolve 3.40 grams of monobasic potassium phosphate KH_2PO_4 (A.C.S. Primary Standard) and 3.55 grams anhydrous dibasic sodium phosphate, Na_2HPO_4, in carbon dioxide-free water and dilute to 1000 mL.

NOTE 2: The Na_2HPO_4 will absorb moisture at relative humidities exceeding about 40% at 25°C and should be dried for two hours at 110-130°C before use. This buffer solution is quite stable when protected from undue exposure to the atmosphere.

6.2.3 *Potassium hydrogen tartrate buffer*, pH 3.56 at 25°C. Add one gram of $KHC_4H_4O_6$ to 100 mL water at about 30°C, shake for several minutes, cool at 25°C, decant, and filter to secure an approximately saturated solution.

NOTE 3: The pH is insensitive to changes of concentration, so elaborate precautions to ensure saturation are unnecessary. The temperature of saturation may vary from 22 to 28°C. Excess solid should be removed as it may cause erratic potentials at the liquid junctions. The tartrate solution is subject to molding accompanied by an increase of pH. Consequently, it cannot be used for more than a few days unless a preservative, such as a crystal of thymol, is added.

6.2.4 *Borax buffer*, pH 9.18 at 25°C: Dissolve 3.81 grams (air-dry weight) of $Na_2B_4O_7 \cdot 10H_2O$ in carbon dioxide-free water and dilute to 1000 mL.

NOTE 4: The dilution value of this solution is so small that changes in the water content of the borax will not affect the pH of the solution. However, exposure to atmospheric carbon dioxide may change its value. It is advisable to replace the solution about a month after preparation.

6.2.5 *Proprietary buffers*, These are permitted provided they are of the proper pH value.

7. Calibration

Before measuring the pH of the specimen solution, calibrate the pH meter at pH 4.01 using the phthalate buffer, and check the phosphate buffer which should have a pH of 6.80 to 6.90. On long runs, check the calibration with a buffer solution having a pH nearest to the measured value of the specimen after measuring approximately every five specimens. After checking, wash the electrode several times with distilled water. The borax buffer and the tartrate buffer may be needed for a specimen with an unusually high or low pH.

8. Sampling

8.1 Obtain a sample of the paper in accordance with TAPPI T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Product."

9. Test specimen

9.1 A composite evaluation is considered appropriate for this test unless otherwise specified.

9.2 Take an equal number of sheets (one or more) from each test unit obtained in accordance with T 400, but not less than a total of five sheets, combining the sheets from all test units. Holding the sheets at one end, cut and crosscut the other end into 5-10 mm squares. Do not include any paper touched with the fingers. From each quantity of cut paper, weigh a test specimen of 1 ± 0.01 g.

9.3 Perform determinations at least in duplicate. In special cases where it is necessary to evaluate different portions of the lot separately, take a portion from each test unit of the sample and perform duplicate determinations on each portion independently, using the same procedure as specified for the composite.

10. Procedure

10.1 Transfer the test specimen to a 125-mL Erlenmeyer flask. Add about 70 mL of distilled water, stir well and attach the condenser.

NOTE 5: Water-cooled condensers are desirable. The air condensers may be used if the temperature of the hot plate can be reduced as indicated below.

10.2 Place the flask on the hot plate. Reduce hot plate temperature as necessary using the hot plate controls and boil gently for one hour, taking care not to exceed the capacity of the condenser. The temperature should be maintained between 98 and 100°C (208 and 212°F).

10.3 At the end of the extraction period cool the flask in running water (to about 35-40°C), with the condenser tube in place and its upper end protected by a loosely fitted small beaker. Replace the condenser with a glass stopper and cool at room temperature. Transfer the mixture to a 100-mL beaker.

10.4 Transfer the extracts for referee or research tests to the 100-mL beakers while hot. Pass nitrogen or CO_2-free air through these extracts while cooling and testing as directed for checking referee water.

10.5 Keep a nitrogen or CO_2-free air cap over the solution during pH measurement. Stir and measure to 0.1 pH unit the pH of the unfiltered mixture according to instructions for the pH meter used.

NOTE 6: Air may be cleaned by passing it through a gas washing bottle containing at least 200 mL of 3N H2SO4 and then through a tower or U-tube containing ascarite or soda lime, 120-150 mm long.

Keep the electrodes, buffer, test solution and wash water at the same temperature and set the compensator for this temperature.

10.6 Before recording the pH, leave the electrodes in the solution until there is no measurable drift in 30 s. Wash the electrodes with distilled water after each measurement and recalibrate frequently.

10.7 For best results, do not use soap or detergent to clean glassware. Use an acid cleaning solution and rinse adequately.

11. Report

Report the average of two determination to the nearest 0.1 pH unit.

12. Precision

12.1 Repeatability (within a laboratory) = 2.4% for comparison of test results from the same test unit, where each test result is the average of two determinations, one each on separate sheets from the same test unit. Repeatability on test results from the same composite sample, as specified in this method should be equal to or smaller than this figure.

12.2 Reproducibility (between laboratories) = 12.3%. The above is the average calculated from data taken from 14 reports on the Collaborative reference program for paper. The above is in accordance with the definitions of these terms in T 1206.

12.3 Comparability = not known.

13. Additional information

13.1 Effective date of issue: March 17, 1988.

13.2 This revision consists of a review and development of precision statement based on data collected from reports on the Collaborative Reference program for paper. It has also been put into the current format for TAPPI test methods.

13.3 Previously, in T 435 m-52, two procedures for pH were given, a cold and a hot extraction. This method is applicable only to hot extractions and should also be differentiated from T 428 which measures the titratable hot water extracted acidity or alkalinity of paper. The changes in this procedure from the previous method are: Specifying additional buffers for calibration and permitting the use of a hot plate.

13.4 It has been found (*2*) that melamine-formaldehyde resin hydrolyzes during hot extraction and releases alkaline products which tend to increase the pH value of the extract. Consequently, when a paper contains both alum and melamine resin, the pH of the hot extract may be higher, or lower than, or equal to a cold extraction value, depending on the relative amounts of alum and melamine resin present.

13.5 The pH of a hot extract of paper sized with rosin and alum is lower than that of a cold extract typically by 0.5 or 0.6 units (*2*).

13.6 Proponents of hot extraction believe that the hydrolysis simulates changes which might occur during natural aging and that values obtained by this method correlate with paper-ink reactions in printing (*3,4*). On the other hand Barrow (*5*) found that cold extraction correlated better with his accelerated aging tests.

13.7 An additional list of reference material for this method is found in *Tappi* **50** (12): 195-A (1967).

13.8 Related methods: ASTM D 778; French AFNOR NFQ 03-005; British Standard 2924; Scandinavian Standard SCAN-P14; Canada CPPA G.25; Australian APPITA-P422.

13.9 This method was revised in 1942, corrected in 1952, and revised in 1968.

Appendix

Treatment of distilled water

A.1 Usually, simple distilled water is satisfactory for use in this method, but the quality of water required is a very important factor. It was found (*6*) that the difference between two lots of water caused a difference of 0.5 pH unit in the extract. Water that does not meet the requirements given in Section 6 should be redistilled.

A.2 Entrained material can usually be removed by redistilling with a high capacity glass still. When distilling from solutions with added chemicals to avoid volatile contaminants, great care must be taken to avoid entrainment. Stills with double heads or traps should be used. Anti-bump

water from a solution containing 1 g of $KMnO_4$ and 4 g of NaOH per liter (*7, 8*). This does not remove ammonia so that any volatile alkalinity is best removed by distilling from very dilute sulfuric acid (*7, 9*).

References

1. ASTM Standard D-1193.
2. Wilson, W. K., Harvey, J. L., and Paddgett, A. A., *Tappi* **34**: 410 (1951).
3. Grant, J., "The Determination of the pH Value of Paper," *BP & BMA. Proc. Tech. Sect.* **36**:473 (1955).
4. *Patra BP & BMA*, **35**: 204 (1954).
5. Barrow, W. J., *Tappi* **46**: 468 (1962).
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7. Taylor, J. E., *J. Chem. Educ.* **37**: 204 (1960).
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Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Test Methods Administrator. ■

T 428 pm-85

TENTATIVE STANDARD—1932
OFFICIAL STANDARD—1940
SUGGESTED METHOD—1967
PROVISIONAL METHOD—1977
REVISED—1985
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Hot water extractable acidity or alkalinity of paper

1. Scope

1.1 This method, based on the work of Kohler and Hall (*1*), measures the titratable acidity or alkalinity (end point at pH 7.0) of an aqueous extract of paper (filtered and extracted by boiling water for 1 h). It specifies one extraction and so does not measure the total acidity or alkalinity of paper, for which exhaustive extraction is required.

1.2 It may be applied to writing, printing, and sized industrial paper but is not intended for testing electrical insulating papers nor those containing alkaline fillers or coatings.

2. Summary

This method consists of a boiling water extraction of the specimen followed by an alkalinity-acidity titration of the extract solution.

3. Significance

The pH determination measures the extent to which the paper alters the hydrogen-hydroxyl ion equilibrium of pure water, and the acidity-alkalinity determination measures the quantity of extracted ionic material that contributes to that equilibrium change. These tests are useful for routine acceptance testing, research work, or the evaluation and classification of different papers.

4. Definitions

4.1 *Paper acidity*, the extent to which water-soluble materials in the paper alter the hydrogen-hydroxyl ion equilibrium of pure water causing an excess of hydrogen ions as measured by titrating with a standardized solution of alkali under specified conditions.

4.2 *Paper alkalinity*, the extent to which water-soluble materials in the paper alter the hydrogen-hydroxyl ion equilibrium of pure water causing an excess of hydroxyl ions as measured by titrating with a standardized solution of acid under specified conditions.

5. Apparatus

5.1 *pH meter*, a commercial pH meter including a glass electrode, reference electrode, and electronic circuitry that will measure emf and indicate pH directly with a precision of 0.01 pH unit (Fig. 1).

5.2 *Erlenmeyer flask*, 500-mL with a 24/40 standard taper joint.

5.3 *Condenser*, West or Allihn type, with 300-mm jacket; or an air condenser about 12 mm OD and 750 mm long; each with a 24/40 standard taper drip-tip joint.

5.4 *Büchner funnel*, 60-mL, glass, with medium fritted disk.

5.5 *Burets*, two 50-mL.

5.6 *Beaker*, 400-mL.

5.7 *Graduated cylinders*, 100- and 250-mL.

5.8 *Hot plate*, preferably with temperature adjustment.

6. Reagents

6.1 *Sodium hydroxide*, 0.01*N* NaOH, accurately standardized (see TAPPI T 610 "Preparation of Indicators and Standard Solutions").

6.2 *Hydrochloric or sulfuric acid*, 0.01*N* HCl or H_2SO_4, accurately standardized (see TAPPI T 610).

6.3 *Distilled or deionized water*, pH 6.8 - 7.3, after having been boiled and protected from CO_2 absorption from the air, requiring not more than 0.5 mL 0.01*N* NaOH for the blank.

6.4. *Carbon dioxide-free gas, nitrogen, or purified air*. Air, if used, should be oil-free. Pass the air through a gas washing bottle containing at least 200 mL of 3*N* H_2SO_4 and then through a tower or U-tube containing ascarite or soda lime, 120-150 mm long, before connecting to the gas dispensing tube.

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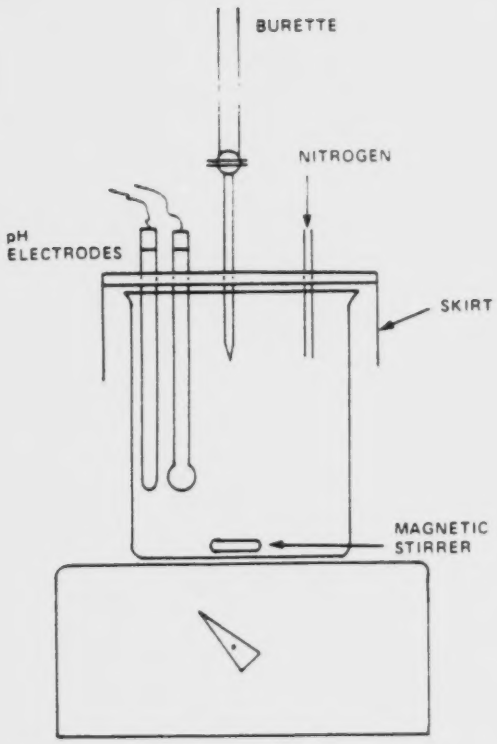

Fig. 1. pH meter.

7. Sampling

Obtain a sample of the paper in accordance with TAPPI T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Product."

8. Test specimen

From each test unit of the sample, cut two representative portions into pieces approximately 5-10 mm square. Keep the portions separate. Allow them to come to equilibrium with the atmosphere near the balance; then weigh out a 5-g test specimen from each portion, each weighed to the nearest milligram. If the moisture content is not known, immediately weigh another specimen and determine its moisture content as described in TAPPI T 412 "Moisture in Paper and Paperboard."

9. Procedure

9.1 Transfer the weighed specimens to the 500-mL Erlenmeyer flasks, add 250 mL of boiling water to each, and attach condensers.

NOTE 1: The air condenser may be used only if the temperature of the hot plate can be controlled.

9.2 Place the flask on a hot plate and boil gently, taking care not to exceed the capacity of the condenser. Heat at this temperature for 60 ± 5 min with occasional shaking. At the end of this period, pour the contents of the flask into the Buchner funnel. Wash with at least 25 mL of hot distilled water. Apply suction to complete the filtration and cool the extract rapidly in a rubber-stoppered Erlenmeyer flask.

9.3 As soon as the extract reaches room temperature, transfer it to a 400-mL beaker, and, using a pH meter, titrate with acid or alkali to a pH of 7.0, while passing nitrogen or CO_2-free air through the specimen as shown in Fig. 1.

9.4 For a blank titration, use 250 mL of distilled water that has been heated for 60 min in the apparatus and filtered following the above procedure.

10. Calculations

For each test specimen calculate the acidity or alkalinity in terms of sulfur trioxide or sodium oxide as follows:

$$\% \ SO_3 = \frac{4N_1 (T_1 - t_1)}{W}$$

$$\% \ Na_2O = \frac{3.1 (T_2N_2 + t_1N_1)}{W}$$

or, if distilled water is greater than pH 7, use this:

$$\% \ Na_2O = \frac{3.1 (T_2N_2 + t_2N_2)}{W}$$

where:

T_1 = volume of alkali required to neutralize extract, mL
T_2 = volume of acid required to neutralize extract, mL
t_1 = volume of alkali required to neutralize the blank, mL
t_2 = volume of acid required to neutralize the blank, mL
N_1 = normality of alkali solution
N_2 = normality of acid solution
W = oven-dry weight of test specimen

11. Report

Express the hot water extractable acidity or alkalinity of the moisture-free paper in terms of the percentage of sulfur trioxide, SO_3, or sodium oxide, Na_2O, to the nearest 0.01%. Report as a test result the average of the two test determinations (i.e., one on each of the two specimens).

12. Precision

12.1 Repeatability (within a laboratory): Duplicate test determinations on low acidity paper on each of three different days in one laboratory agreed to 0.01% acidity. It is estimated from this limited information that repeatability of test results for low acidity paper would be about 0.02% acidity.

12.2 Reproducibility (between laboratories): not known.

12.3 The above terms are used in accordance with the definitions in TAPPI T 1206 "Precision Statement for Test Methods."

13. Additional information

13.1 Effective date of issue: March 27, 1985.

13.2 This revision includes a precision statement, and the method is written in the current format for TAPPI Test Methods.

13.3 A hot extract of paper is usually more acid than a cold extract (*2*). This is caused by hydrolysis of the aluminum compounds retained in the paper. It has also been found (*3*) that alkaline products are released by the hydrolysis of melamine-formadehyde resins during hot-water extraction.

13.4 This method was corrected or revised in 1936, 1939, 1945, 1967, and 1977.

13.5 Related methods: ASTM D548; SCAN P14; TAPPI T 435; CPPA G 25.

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Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Test Methods Administrator. ■

T 452 om-87
SUGGESTED METHOD – 1941
TENTATIVE STANDARD – 1945
OFFICIAL STANDARD – 1977
OFFICIAL TEST METHOD – 1983
REVISED – 1987
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Brightness of pulp, paper, and paperboard (directional reflectance at 457 nm)

1. Scope

1.1 This method is for the determination of the brightness of white, near-white, and naturally colored pulp, paper, and paperboard. Brightness is a commonly used industry term for the numerical value of the reflectance factor of a sample with respect to blue light of specific spectral and geometric characteristics. This method requires an instrument employing 45° illumination and 0° viewing geometry with the illuminating and viewing beams adjusted so that translucent materials are evaluated on an arbitrary but specific scale. The cone of light (see A.3.2 and A.3.5) used by this method is wider than that specified for the CIE Standard 45/0 geometry.

1.2 This procedure is applicable to all naturally-colored pulps, and papers and board made therefrom. The measurement is not suitable for paper or paperboard containing added coloring matter (such as yellow or green dyestuff) which appreciably absorbs light in that part of the spectrum extending from about 400 to 500 nm. Colored papers must be measured either spectrophotometrically or colorimetrically in order to obtain meaningful results (*1*).

1.3 This method gives:

1.3.1 A procedure for using the test instrument to measure the directional reflectance factor at 457 nm of a sample of paper or paperboard (*2-5*).

NOTE 1: The effective wavelength of the spectral band is 457 nm. The shape of the function is also important and is defined in Appendix A.

1.3.2 A procedure described in Appendix C for separating the fluorescent component of brightness from the non-fluorescent component of brightness and measuring it quantitatively.

1.3.3 A description of a system of preparing, distributing and using reflectance standards by which an instrument can be maintained in continuous agreement, to within specified tolerances, with a master instrument.

1.3.4 A detailed description (Appendix A) of the significant spectral, geometric, and photometric characteristics of a master instrument to be maintained in a central standardizing laboratory[1], with a statement of the tolerances which must be met in its construction and maintained during its use.

2. Summary of method

This method provides: (a) a scale for measurement of blue directional reflectance factor, (b) a method for verifying the calibration of each instrument used for reflectance testing so that the user can rely upon the test results, and (c) criteria by which to judge whether any instrument (differing in optical, geometric, and photometric characteristics from the master instrument) may safely be employed in performing this reflectance test.

3. Reflectance scale and standards

3.1 *Reflectance scale:* The standard brightness scale is based on the reflectance of magnesium oxide of 100.0%. This scale is rigorously maintained by the Institute of Paper Chemistry utilizing instrumental methods not dependent upon unstable physical standards such as magnesium oxide (*6*).

3.2 *Standards:* Sets of paper tabs and polished white opal glass standards shall be supplied by the central standardizing laboratory[1] with calibrations based on the master instrument. Sets of at least five pads of paper and two opal glass standards shall be provided.

[1]Central standardizing laboratory: Institute of Paper Chemistry, Appleton, WI, 54912, USA.

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4. Apparatus

4.1 *Brightness tester*[2], a test instrument of such design and in such adjustment that its calibration is correct to within the tolerances specified in 5.1.

NOTE 2: Identity of reading with that of the master instrument on one or two pads of standards is not sufficient proof that readings on the test instrument and on the master instrument will be identical on all samples, even though the test instrument gives brightness values very close to those assigned to the standards. The test instrument will be in proper calibration if it reads all standards within ± 0.3 point of their assigned values.

4.2 *Standards*, a set of five pads of paper tabs and two opal glass standards as described in 3.2 and Appendix B.

4.3 *Backing weight*, 1-kg weight with flat bottom.

5. Calibration

5.1 Obtain reflectance standards supplied by the central standardizing laboratory[1] (see Appendix B) at monthly intervals and calibrate the test instrument with them as soon as they are received. If the instrument readings on the standards differ from their assigned value by more than ±0.3 point, adjust the instrument in accordance with the manufacturer's instructions so that the readings agree with the assigned values to within 0.3 point.

5.2 Check the test instrument readings periodically against the assigned values of all the standards. A frequent check should be made with the opal glass standard and the paper standard nearest the brightness range of interest. The frequency of these checks will depend on the amount of use of the instrument and the accuracy required. Care should be exercised that the paper standards do not become soiled through frequent use.

5.3 At intervals of one to three years, depending upon the conditions and frequency of use, the test instrument should be disassembled and carefully inspected, tested, and adjusted to insure that its geometric and spectral characteristics fall within prescribed limits, and that its photometric system is within the specified tolerances.

6. Test specimens

6.1 *Sample preparation—paper and paperboard*

6.1.1 Sample the material to be tested in accordance with TAPPI T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Product." From each test unit cut a representative portion of the paper or board into seven or more tabs at least 30 mm longer and 20 mm wider than the specimen aperture [nominally 51 mm (2 in.) by 38 mm ($1\frac{1}{2}$ in.) with the short dimension parallel to the machine direction]. Avoiding any water mark, dirt, or blemish, assemble the tabs in a pad with the top sides up. Use the top tab as a cover only; mark it near one corner to identify the sample and the top side. More than seven specimen tabs may be required for thin or transparent samples to ensure that the pad is completely opaque. (Only a few tabs will be required for paperboard.) The number of tabs in the pad should be such that the measured reflectance is not changed by doubling its thickness.

6.1.2 Do not touch test areas of the specimen with the fingers. Protect the test areas from contamination, excessive heat, or intense light.

6.2 *Sample preparation—pulp.* Prepare sheets from pulp samples in accordance with TAPPI T 218 "Forming Handsheets for Reflectance Tests of Pulp."

7. Procedure

7.1 Without touching the test areas with the fingers, remove the protective cover tab and place it at the back of the pad. Place the pad over the specimen aperture of the instrument with the machine direction of the paper parallel to the plane determined by the axes of the incident and reflected rays of light and with the top side in contact with the instrument. If an orientation effect is suspected (as in the testing of creped or embossed specimens), rotate the pad and observe the highest and lowest readings. Clearly record in the report how the specimens are oriented and the reading for each orientation.

7.2 Place the 1-kg backing weight on the pad. Measure and record the reflectance reading to 0.1 unit.

7.3 Move the lower tab to the back of the pad and measure the second tab. Repeat this procedure until five tabs have been measured.

8. Report

Report the average brightness of the sample to one decimal place, together with the minimum and maximum readings. State clearly and conspicuously any deviations from the standard procedure, and note any unusual features or characteristics of the sample.

9. Precision

Data on the precision of measurement have been obtained from the published reports of the TAPPI-NBS Collaborative Reference Program (7), in which approximately 20 laboratories participated. The directional blue reflectance factor values ranged between 60 and 87. The within-laboratory repeatability and the among-laboratory reproducibility were computed from the averages of the reported standard deviations in accordance with TAPPI T 1206 "Precision Statement for Test Methods":

Repeatability: 0.3
Reproducibility: 1.3

10. Additional information

10.1 This method incorporates previous method TAPPI T 217 "Brightness of Pulp." This method was corrected in 1947 and revised in 1942, 1948, 1958, and 1977.

10.2 Effective date of issue: July 29, 1987.

10.3 Related methods: Scandinavian SCAN P3:75, SCAN C11:75, SCAN G1:75, Canadian E.1; ISO 2469, 2470; TAPPI T 525 "Diffuse Blue Reflectance of Pulp (Diffuse Brightness)," T 534 "Diffuse Blue Reflectance Factor for Clay and Mineral Pigments (Diffuse Brightness),"

[2]Names of suppliers of testing equipment and materials may be available from the TAPPI Information Resources Administrator.

T 646 "Brightness of Clay and Other Mineral Pigments (0°–45° Directional)."

10.4 Appendix C, Fluorescent component of brightness, was added in 1987.

References

1. TAPPI T 442 "Spectral Reflectance Factor, Transmittance and Color of Paper and Pulp (Polychromatic Illumination)," T 524 "Color of White and Near-White Paper and Paperboard by *L, a, b* 45° 0° Colorimetry," and T 527 "Color of Paper and Paperboard in CIE System."
2. Instrumentation Studies XIII, *Paper Trade J.* **104** (18):47;(19):51; (20):45 (1937); XX, *Paper Trade J.* **105** (18):135; (19):27 (1937); XXI, *Paper Trade J.* **105** (25):46 (1937); XXII, *Paper Trade J.* **105** (27):42 (1937); XVIII, *Paper Trade J.* **107** (20):33 (1938); XXIX, *Paper Trade J.* **107** (25):29 (1938); XXXVII, *Paper Trade J.* **112** (1):13 (1941); LVIII, *Tappi* **33** (10):85 (1950); LXV, *Tappi* **34** (9):143A (1951); LXIV, *Tappi* **34** (8):126A (1951); LXXVI, *Tappi* **35** (11):141A (1952); LXXXIV, *Tappi* **41** (9):196A (1958); LXXXV, *Tappi* **43** (2):230A (1950); LXXXVI, *Tappi* **43** (5):253A (1960); LXXXVII, *Tappi* **46** (1):179A (1963); Van den Akker, J.A., Nolan, P., and Wink, W.A., "The Physical Basis of Standardization of Brightness Measurement," *Paper Trade J.* **114** (5):34 (1942); Van den Akker, J.A., "Wavelength Calibration of Spectrophotometers," *J. Opt. Soc. Am.* **33** (5):257 (1943).
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7. Collaborative Reference Program for Paper (TAPPI), Report Nos. 10 through 48, October 1970 to June 1977.

Appendix A. Master Instrument

A.1 The master instrument is defined by spectral, geometric, and photometric characteristics as follows:

A.2 *Spectral characteristics*

A.2.1 The effective wavelength of the instrument, when used with the filter required for this standard is 457.0 ±0.5 nm. The effective wavelength is that wavelength of monochromatic light for which the transmittance of a filter having a spectral transmittance given by the equation $T = a + b\lambda$ is equal to that determined with a master instrument, after a correction is made for effects associated with refraction and reflection, angular spread of rays through the filter, photometric error, and the wavelength error in the spectrophotometer employed to determine the spectral transmittance. In this equation, which need hold only for that wavelength range transmitted by the brightness filter, T is transmittance, a and b are constants, and λ is the wavelength. Filters having positive and negative b values should be employed so that, by averaging the two effective wavelength determinations, the correct effective wavelength will be obtained even though a photometric error may be present. Differences between the two values can be related to the photometric error which in the master instrument is not greater than 0.1%. A suitable correction should be applied if a photometric error exists. The spectral transmittance of the linear filter is measured relative to a clear, nonabsorbing plate of equal thickness and similar index of refraction. The spectral transmittance is so measured in both the master instrument and the spectrophotometer, and the filters are so disposed with respect to apertures as to minimize error due to scattering of light in the filters and to make such error as may be due to light scattering the same in the master instrument and the spectrophotometer.

A.2.2 The spectral power distribution of the light incident on the specimen determines the response of the instrument to fluorescent radiation which may be caused by the presence of fluorescent whitening agents. The product of the spectral power distribution of the source and the spectral transmittance of the glass lenses and filter in the incident system is $E(\lambda)$, where $E(\lambda)$ is the function of wavelength given in Table 1.

Table 1. Relative spectral energy distribution of the light incident on the specimen; color temperature of the light source is 3000K.

Wavelength, nm	E(λ) relative units
320	0.0
330	0.7
340	3.0
360	9.7
380	17.1
400	26.0
420	37.2
440	50.3
460	64.1
480	80.0
500	100.0

A.2.3 The effective wavelength, 457.0 ± 0.5 nm is obtained by the combination of illuminant, glass optics, filters, and photodetector for which the mathematical product of relative spectral power distribution, spectral transmittance, and spectral response is $F(\lambda)$, where $F(\lambda)$ is the function of wavelength given in Table 2. The area under the curve which represents the product for all wavelengths greater than 700 nm of the spectral sensitivity of the photoelectric cell, and the spectral transmittance of all filters between the specimen aperture and the photoelectric cell, is so small compared with a similar area for the wavelength range 360 to 510 nm that no detectable part of the photoelectric current may be ascribed to infrared fluorescence of the test specimen.

Table 2. Product of relative spectral power distribution of illuminant, spectral transmittance of glass optics, spectral transmittance of all filters and the spectral response of the phototube (or photocell)

Wavelength, nm	P_λ, relative units
395	0.0
400	1.0
405	2.9
410	6.7
415	12.1
420	18.2
425	25.8
430	34.5
435	44.9
440	57.6
445	70.0
450	82.5
455	94.1
460	100.0
465	99.3
470	88.7
475	72.5
480	53.1
485	34.0
490	20.3
495	11.1
500	5.6
505	2.2
510	0.3
515	0.0

A.3 *Geometric characteristics*

A.3.1 The mean angle of incidence of light rays upon the test specimen is 45 ±0.5°.

A.3.2 The incident rays upon a point of the test specimen are confined within a cone having a half angle of 11.5 ± 2°. This cone is filled with light, has its vertex in the specimen aperture, and has its base at the emergent aperture of the condensing lenses.

A.3.3 The specimen aperture is circular with a diameter of 12.7 ±0.13 mm (0.500 ±0.005 in.). The exit aperture of the optical system which accepts reflected rays for measurement is concentric and parallel to the specimen aperture and has a diameter of 9.53 ±0.076 mm (0.375 ±0.003 in.) so that light reflected from the rim of the specimen aperture does not reach the photoelectric cell.

A.3.4 The mean angle of rays reflected by the test specimen and accepted by the receiving optical system for measurement is between 0° and 0.5° with the normal to the plane of the specimen aperture.

A.3.5 The reflected rays accepted for measurement are confined to a cone having a half angle of 22.5 ±2°.

A.4 *Photometric characteristics*. The instrument shall incorporate a photometric measurement system which measures reflectance in direct proportion to the light energy incident upon the sample within 0.1% throughout the entire range of measurement. Suitable checks must be made by the central standardizing laboratory to ensure the long-term stability of the spectral, geometric, and photometric characteristics of the master instrument.

Appendix B. Calibration service

B.1 The central standardizing laboratory to which is delegated the responsibility of maintaining and operating the calibration service will distribute standards on a monthly basis to all subscribers. A set of standards will comprise at least five pads of paper tabs and two white opal glass standards with brightness values accurately established by measurement on the master instrument.

B.2 The paper standards will cover a range from about 50 to 90% reflectance. The paper from which these standards are prepared will be white or cream colored, have a fairly stable and uniform reflectance, and a relatively smooth but not supercalendered surface. At least one standard will contain a fluorescent whitening agent.

NOTE 3: Paper standards are satisfactory for calibration of instruments used for measurement of pulp, paper, or paperboard.

B.3 The opal glass standards shall have a surface not deviating from a true plane by more than 0.025 mm (0.001 in.). The nature of the surface polish and hardness and the optical stability of the material shall be such that the reflectance during one month of intensive but careful use will not vary more than 0.3 point, and such that it may be easily and effectively cleaned and be sufficiently resistant to withstand several cleanings per day. The color of the opal glass standards will be white or cream with the maximum spectral reflectance not more than twice the minimum over the wavelength range of 400 to 500 nm. The opal glass standards shall be non-fluorescent.

Appendix C. Fluorescent component of brightness

C.1 *Scope and significance*

C.1.1 The purpose of the procedure in this appendix is to describe a method for separating the fluorescent component of brightness from the non-fluorescent component and measuring it quantitatively.

C.1.2 When brightness is measured in accordance with the procedures outlined in this method, the specimen is illuminated with a broad spectrum of light, and the blue reflectance is measured. If the material contains natural or added fluorescent brighteners, a higher brightness reading will be obtained than if no fluorescence were present. The brightness reading, therefore, includes a "non-fluorescent component" and a "fluorescent component."

C.1.3 Fluorescence is stimulated when radiation of short wavelength (often ultraviolet, violet, and blue light) is partially absorbed in electronic processes that yield visible light or infrared radiation. If no short wavelength light strikes the specimen, no fluorescence in the blue region of the spectrum is excited.

C.1.4 Figure 1 shows a simplified diagram of the illumination and viewing system of a brightness tester in its normal configuration. Ultraviolet and visible light are allowed to illuminate the specimen, and reflected light is passed through the brightness (blue) filter before striking the photocell. The brightness reading, therefore, includes the visible blue light reflected by the specimen, plus additional blue light which was excited by the ultraviolet light in the incident beam.

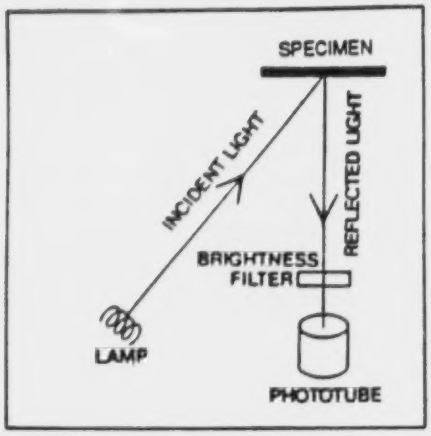

Fig. 1. Normal configuration for brightness measurement. Fluorescence is excited and read if present.

C.1.5 The brightness filter, referred to in C.1.4, consists of several component filters placed together. If the ultraviolet absorbing component of the brightness filter has been moved from the reflected beam to the incident beam (Fig. 2), the overall spectral response of the instrument (Table 1) remains unchanged, but it prevents the passage of ultraviolet light and allows only the visible blue light to illuminate the specimen and reflect into the photocell. If no fluorescence is present, the brightness reading will be the same regardless of whether the ultraviolet absorbing component of the filter is in the incident beam or the reflected beam. If fluorescence is present, the readings will differ, the difference being the amount of light contributed by the "fluorescent component." For example, if a brightness reading of 90.0 is obtained using the normal configuration in Fig. 1 and a brightness of 85.0 is obtained using the Fig. 2 configuration, then the "fluorescent component" is equal to 5.0 or 5 "brightness points."

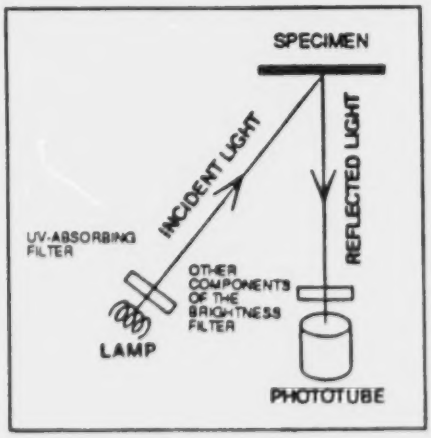

Fig. 2. The UV-absorbing component of the brightness filter is moved to the incident beam eliminating ultraviolet illumination of the specimen. Fluorescence is not excited and only the "non-fluorescent" component of brightness is read.

C.2. *Apparatus. Brightness tester*, a test instrument equipped with fluorescence separation capability and in such adjustment that it correctly measures the fluorescent component of the paper standard provided by the central standardizing laboratory[1] within ±0.3 brightness units. Other criteria are:

C.2.1 The filters must be selected such that the effective wavelength of the overall brightness function (Table 2) does not change more than ±1.5 nm when the UV absorbing filter is moved from the receiving to the incident light beam. Likewise the bandwidth must not change more than ±3 nm under the same conditions.

C.2.2 The instrument response in the red (600–700 nm) region of the spectrum must not exceed 0.2 reflectance units.

C.2.3 The "fluorescent component" measured on the non-fluorescent paper and opal glass standards must not exceed 0.2 brightness units.

C.2.4 Brightness is defined such that the measured quantity is independent of the illuminant. This does not hold for specimens containing optical brighteners as the degree of fluorescence excitation is directly related to the spectral energy distribution of the light incident upon the specimen. The relative spectral energy distribution of the light incident on the specimen will be changed from that shown in Table 1 to that shown in Table 3 by the movement of the UV absorbing filter from the receiving to the incident beam. The spectral distribution of the energy incident upon the specimen must be sufficiently matched to that shown in Table 3 to correctly measure the fluorescent paper standard provided by the central standardizing laboratory[1] within ±0.3 brightness units.

C.3. *Test specimen.* For sample preparation, see Section 6.1.

C.4. *Procedure*

C.4.1 Calibrate the instrument for brightness measurement in accordance with the procedure described in the manufacturer's instruction manual.

C.4.2 Without touching the test areas of the specimens with the fingers, remove the protective cover tab, placing it at the back of the pad, then place the pad over the test aperture of the instrument with the machine direction of the paper parallel to the plane determined by the axes of the incident and reflected rays of light, and with the felt or

Table 3. Relative spectral energy distribution of the light incident on the specimen with the UV absorbing filter in the incident light beam (Fig. 2)

Wavelength, nm	*E(λ) relative units*
380	0
400	1.0
420	8.2
440	22.4
460	45.3
480	71.7
500	100

topliner side facing the instrument. Place the 1-kg weight upon the pad. Measure and record the reading to 0.1 unit. Move the lower tab to the back of the pad and take another reading. Repeat this procedure until five different tabs have been tested. Designate the readings as R_1.

C.4.3 Set the filter selector to the designated position where the non-UV-absorbing components of the brightness filter are in the reflected beam and insert the matching ultraviolet absorbing component of the brightness filter into the incident beam.

C.4.4 Set the opal glass standard over the specimen apeture and, if necessary, adjust to the standard value.

C.4.5 Place the specimen over the test aperture and take a reading. Record the reading and repeat until values have been obtained for 5 tabs. Designate these readings as R_2.

C.5. *Calculations*

C.5.1 Average the readings taken in step C.4.2 to obtain R_1.

C.5.2 Average the readings taken in step C.4.5 to obtain R_2.

C.5.3 Calculate the fluorescent component in accordance with the formula:

$$\text{Fluorescent component} = R_1 - R_2$$

C.6. *Report.* Report the fluorescent component value obtained in Section C.5.3 to the nearest 0.1%.

C.7. *Precision.* The precision values are the same as in Section 9.

C.8. *Additional information*

C.8.1 This method can also be used to evaluate the fluorescent component of reflectance for functions other than brightness, such as the tristimulus function Y, provided multi-component filters for these functions are available.

C.8.2 The ratio of ultraviolet to blue light energy illuminating the specimen must be closely controlled from instrument to instrument in order to obtain good interlaboratory agreement with this method. This ratio is set to the same value in every instrument of the type specified in C.2 and is checked through the monthly brightness standardization service.

C.8.3 Visual assessment of fluorescence is dependent upon the conditions of illumination. The degree of agreement between fluorescence values determined by this method and by visual assessment depends on the closeness of match between the UV/blue ratio of the light source employed for visual assessment and the UV/blue ratio of the illuminant specified in this method. Relative rankings of fluorescent specimens by this method correlate directly with relative rankings obtained by visual assessment regardless of the standard illuminants employed.

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Technical Divisions Administrator.

CAUTION:
This method may require the use of some chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Material Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this test method, the user should determine whether any of the chemicals to be used are potentially hazardous and, if so, should follow strictly the procedures specified by both the manufacturer, as well as state and federal authorities, for safe use of these chemicals.

T 430 om-88

TENTATIVE STANDARD – 1932
OFFICIAL STANDARD – 1942
SUGGESTED METHOD – 1968
OFFICIAL STANDARD – 1975
OFFICIAL TEST METHOD – 1983
REVISED – 1988

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Copper number of pulp, paper, and paperboard

1. Scope and significance

1.1 This method describes a procedure for determining the copper number of bleached and purified pulp, paper, and paperboard, except those containing calcium sulfite, zinc sulfide, melamine resin, or other copper-reducing nonfibrous materials. Papers containing such additives can be tested only if the amount and reducing power of the added material is known.

1.2 It has been well established that hydrolyzed or oxidized cellulose is capable of reducing certain metallic ions to lower valence states, and reactions of this type have served to detect damage to cellulose and to estimate the quantity of reducing groups.

1.3 The copper number may be regarded as an index of those impurities in paper, such as oxycellulose, hydrocellulose, lignin, and sugars, which possess reducing properties. It is useful for determining changes accompanying deterioration and may therefore be considered as a factor having an indirect bearing on the permanence of paper. It should not be applied to papers containing mechanical pulp or unbleached chemical pulp.

2. Definition

Copper number is defined as the number of grams of metallic copper (as Cu_2O) resulting from the reduction of $CuSO_4$ by 100 g of the pulp or paper fibers.

3. Apparatus

3.1 *Grinder*,[1] which will disintegrate the pulp and paper fibers without appreciably heating, contaminating, or deteriorating them. A Koerner-type grinder or its equivalent has been found satisfactory. After disintegrating, the sample should have an absorbent cotton-like appearance.

NOTE 1: If a Koerner grinder is not available, a small Hammermill or other laboratory equipment may be used to fluff the test portion, provided the cellulose is not degraded as measured by a decrease in CED viscosity [see T 230 "Viscosity of Pulp (Capillary Viscometer Method)"].

3.2 *Bath*, a steam or oil bath maintained at 100° ± 1°C.

3.3 *Büchner funnel*, 75 mm, with suction flask, 1000 mL.

3.4 *Glassware*, graduated cylinders, 10, 25, 100, 250, and 500 mL; volumetric flask, 100 mL; Erlenmeyer flask, 125 mL, with loosely fitting glass bulb or stopper; glass rod with flattened end; beaker, 100 mL; buret, 50 mL; and wide-mouth jar with screw cover.

3.5 *Mixer*, high-speed, to slurry the pulp with water.

3.6 *Miscellaneous*, 100-mm ashless filter paper.

4. Reagents

4.1 *Copper sulfate solution.* Dissolve 100 g $CuSO_4 \cdot 5H_2O$ in water and dilute to 1000 mL.

4.2 *Carbonate-bicarbonate solution.* Dissolve 350 g $Na_2CO_3 \cdot 10H_2O$ (or 129 g of anhydrous Na_2CO_3) and 50 g $NaHCO_3$ in water and dilute to 1000 mL.

4.3 *Phosphomolybdic acid* (molybdophosphoric acid) solution. Dissolve 100 g of sodium molybdate, $Na_2MoO_4 \cdot 2H_2O$, and 75 mL of phosphoric acid (85%) in a mixture of 275 mL concentrated H_2SO_4 and 1750 mL of water.

NOTE 2: Always add acid to water, not water to acid.

[1] See separate TAPPI list of suppliers of testing equipment and materials available for this method.

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4.4 *Sodium carbonate*, an approximately 5% Na_2CO_3 solution.

4.5 *Potassium permanganate*, 0.05*N* $KMnO_4$ (see T 610 "Preparation of Indicators and Analytical Reagents, and Standardization of Volumetric Solutions" for preparation and standardization).

5. Sampling and test specimens (pulp)

5.1 Obtain a sample of the pulp in accordance with a previously determined sampling procedure. Select a representative test portion of at least 10 g dry basis.

5.2 Add the portion to distilled water and slurry it until thoroughly separated, then filter on a paper in the *Büchner* funnel with suction, and finally air-dry.

NOTE 3: Take care to minimize loss of fines. This loss will substantially lower the copper number.

5.3 After air-drying, "fluff" the portion by passing it through the grinder, then place into a wide-mouth jar and seal.

5.4 Allow the fluffed pulp to equalize in moisture content, then weigh out two test specimens each of about 1.5 g (to the nearest 0.01 g) and transfer each to a 125-mL Erlenmeyer flask. In addition, make moisture and ash determinations in accordance with T 210 "Sampling and Testing Wood Pulp Shipments for Moisture" and T 211 "Ash in Wood and Pulp," respectively.

6. Sampling and test specimens (paper and paperboard)

6.1 From each test unit obtained in accordance with T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Product" take approximately equal portions (5-10 g), representative of each test unit, and combine into a single composite sample.

6.2 If nonfibrous material may be present, make qualitative tests for them before weighing portions of the sample for test. Examples are: sizing materials such as rosin, starch, glue, and casein; saturants such as waxes; mineral fillers, especially calcium sulfite and zinc sulfide. Do not attempt to apply this procedure if copper-reducing substances are found.

6.3 If the paper is *coated* using a *casein* binder, the coating may be removed in accordance with UM 542 "Amount of Coating on Mineral-Coated Paper". Air-dry the decoated paper before proceeding. UM 542 is *not* applicable to latex bound coatings.

6.4 Disintegrate the sample in the grinder.

6.5 Allow the ground composite sample to come to moisture equilibrium with the atmosphere of the balance for at least 1 h. Weigh at least two 1.5-g specimens of the ground paper to the nearest 0.01 g and transfer each to a 125-mL Erlenmeyer flask. At the same time weigh specimens and make determinations for moisture (see T 412 "Moisture in Paper and Paperboard"), ash (see T 413 "Ash in Paper and Paperboard"), and nonfibrous noncopper reducing materials [see T 408, "Rosin in Paper and Paperboard"; T 419 "Starch in Paper"; T 504 "Glue in Paper (Qualitative and Quantitative Determination)"; UM 490 "Casein and Soya Protein in Paper (Qualitative)"; T 405 "Petroleum Wax in Impregnated Papers"; and T 421 "Qualitative (Including Optical Microscopic) Analysis of Mineral Filler and Mineral Coating of Paper"].

7. Procedure

7.1 Immediately before use, add 5.0 mL of $CuSO_4$ solution (4.1) to 95 mL of the carbonate-bicarbonate solution (4.2). Heat the mixture to a boil in 2 min, and pour it into the flask over the test specimen. Stir well with a glass rod in order to distribute the fibers and to remove air bubbles. Fit the flask with a loosely fitting glass bulb or stopper and submerge it just above the liquid line in the steam or oil bath. Since fibers tend to float to the surface, shake the flask from time to time to redistribute them.

NOTE 4: The amount of solution (4.1) given above is sufficient for a copper number not greater than 6. This figure is seldom exceeded except with pulps and papers containing highly lignified fibers, such as groundwood, to which this method does not apply, or for pulps and papers which have deteriorated considerably. If the copper number exceeds 6, increase the volume of copper sulfate solution (4.1) to 10 mL and subsequently, the volume of molybdophosphoric acid solution (4.3) to 50 mL or more (to maintain the $^1/_5$ ratio).

7.2 At the end of 3 h, remove the flask from the bath. Filter on an ashless filter paper in the Büchner funnel, with suction. Wash by flooding with 100 mL of the 5% Na_2CO_3 solution (4.4) at about 20°C and then by flooding with 250 mL of hot water at about 95°C. Discard the filtrates. Transfer the fibers and filter paper to a 100-mL beaker, add 25 mL of the molybdophosphoric acid solution (4.3) and macerate well with a flattened glass rod. Transfer to a clean Bu..chner funnel fitted with an ashless filter paper and wash thoroughly with cold water, collecting the filtrate, until all the blue color is removed.

NOTE 5: This final wash should be completed within 30 min because it becomes increasingly difficult to wash the blue molybdenum oxide color from the fibers as time proceeds, resulting in abnormally low copper number values.

7.3 Dilute the filtrate with water to approximately 700 mL and titrate it with 0.05*N* $KMnO_4$ (4.5) to a faint pink which persists for 30 s.

7.4 Make a blank determination following the same procedure using the same amounts of reagents and water.

8. Calculation

Calculate the copper number on the basis of 100 g of moisture-free sample by the following formula:

$$\text{Copper number} = 6.36\ (V - B)\ N\ /\ W$$

where:

V = $KMnO_4$ solution to titrate the filtrate from the specimen, mL
B = $KMnO_4$ solution to titrate the blank filtrate, mL
N = normality of $KMnO_4$ solution
W = moisture-free weight in grams of the test specimen, after subtracting the weight of ash and other noncopper reducing nonfibrous components whenever they are present in significant amounts

9. Report

Report the copper number as the average test result of the two determinations, to one decimal place.

10. Precision

10.1 Repeatability (within laboratory) = 10%;

10.2 Reproducibility (between laboratories) = not known;

10.3 The estimate of repeatability is based upon a total of 36 determinations made in one laboratory on three different pulps.

11. Additional information

11.1 Effective date of issue: March 17, 1988.

11.2 This method is essentially the Braidy (*1*) modification of the original Schwalbe (*2*) method, with modifications for its adaption to paper proposed by Scribner and Brode (*3*) and by Burton and Rasch (*4*).

11.3 The Enka method as described by Morgan and Henry (*5*) was evaluated in the laboratory and found not to be more precise for pulps and to give a different level of values from this method.

11.4 It has been found (*6*) that melamine-formaldehyde resin in paper produces a decrease (0.2 - 0.4) in the copper number of paper. Some unpublished research work indicates that urea-formaldehyde resin gives an increase of 0.2 - 0.4 in the copper number of paper.

11.5 The work of Shaw et al. (*7*) indicates that glue and starch sizings increase the copper number of paper by about 0.05 copper number unit; also rosin size, used with alum, was found to increase the copper number in the order of 0.2 copper number unit.

11.6 Related methods: ASTM D919; Scandinavian SCAN C-22 (semi-micromodification); Canadian CPPA G.22 (substantively similar); German VZPCI 8.

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Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Test Methods Administrator. ■

SECTION V

PHYSICAL EFFECTS

V. PHYSICAL EFFECTS

Initial increases in measured physical characteristics of treated paper (prior to aging) is an indication of strengthening effects. Newer papers will generally show significantly less enhancements than older material. While it is generally known that the tensile strength is a poor measure of aging stability other tensile properties give important information. It has been further observed that the MIT fold number and tearing resistance are sensitive indications of the aging of paper. Folding endurance is more sensitive to changes in the structural properties of paper than any other strength measurement. The differences in the physical measurements between treated and untreated paper over a specified aging time frame gives insight into the projected book life extension due to treatment. The effects can be measured by the following procedures.

A. Folding Endurance

Through normal use, book paper is exposed to repeated foldings and its ability to resist such stresses is an extremely important feature. Different instruments have been devised to evaluate this property. However, they do not all necessarily produce the same result. One reason for this is the different folding angles of the different apparatus. Generally the fold number decreases 2-4% per degree of bend. Essentially a paper strip is quickly folded under a certain applied tensile stress until it breaks. A disadvantage of these tests is the amount of scatter in the results obtained. This outcome is the result of the test methods employed. The strip is forced to break in a certain predetermined area, rather than at its weakest point. Hence small, local structural variations in the paper have a considerable effect on the result.

The MIT folding endurance test, TAPPI T-511, is used to measure the ability of paper to maintain its strength after repeated folding. In the MIT folding endurance test, the specified test uses a 1 kg weight on the folding sample. For many book papers and even some office papers, this weight gives results of only a few folds, making the loss on aging difficult to measure. It has been found that reduction of the weight to 500 grams gives much larger numbers for the initial fold and therefore provides a relatively large span over which to measure the loss on aging. The values with a 500 g load are just as valid as those with a 1 kg load, and the standard deviation is comparable.

Hence the folding endurance is measured according to TAPPI Standard T-511 using a MIT fold tester. The tension is set to 0.5 kg (4.9N) using a weight. The test strips are cut to 15 mm-wide parallel strips within ± 0.03 mm with clean edges; the length is not less than 130 mm. Record the number of double folds to breakage. Calculate the mean and report as MIT folding endurance to three significant figures. **For any acidic paper, on the basis of a minimum of 10 test strips, selected at random, the folding endurance value of treated versus untreated strips shall not average less than 3x after 28 days of accelerated aging.** It is useful to compute the standard deviation of the test to provide a measure of the significance of the differences in folding endurances of the different samples.

B. Tear Resistance

The Elmendorf tear test, TAPPI T-414, measures the internal tearing resistance of paper. Internal tearing resistance is a measure of the force perpendicular to the plane of the paper necessary to tear a single sheet through a specified distance after the tear has already been started.

TAPPI T-470 describes the procedure for evaluating the edge-tear strength of paper. Edge-tearing strength is a measure of the force needed to initiate a tear. The force necessary to start a tear is greater than the internal tear resistance. The out of plane tearing mode, used in the Elmendorf test, resembles the type of tearing that occurs when a nicked sheet in a book is accidentally torn by a reader while turning pages.

The Elmendorf tear test, TAPPI T-414, is to be performed as specified on treated and untreated paper. **The values are to be reported for the indicated paper types before and after 28 days of accelerated aging. The average values for treated paper should be significantly higher than the average values for untreated paper after this interval.**

C. Tensile Analysis

Tensile strength can be measured by TAPPI Test T-494. This method measures the tensile breaking properties of paper using a constant rate of elongation instrument. Tensile stress-strain curves provide fundamental engineering behavior of paper when subject to tensile stress. A stress-strain curve in which the initial slope is high, where there is little curvature, and where the value for elongation to break is low, indicates a brittle material. A tough material is one that exhibits more viscoelastic behavior, a pronounced curvature, and a high elongation to break. Hence a comparison of curves for treated and untreated, aged and unaged paper sample gives insight into the strengthening characteristics imparted by a process. The sample should be selected as specified in TAPPI T-400 and conditioned in accordance with TAPPI T-402. One variation is to measure the tensile strength following a defined fold as described in the attached article by H. Bansa.

Tensile strength studies are accomplished with an Instron apparatus using a modified TAPPI Method T-494. The samples are cut to 25 mm wide parallel strips within ± 0.02 mm with clean edges. The paper is placed in the jaws of the tester at a 180 mm span and pulled at 1.25 mm/min. to breakage. The tensile strength, tensile energy absorption (toughness), yield point, and Young's Modulus are reported. Tensile energy absorption quantifies the durability of a material subjected to repeated stress. Youngs Modulus is a measure of the stiffness of the paper. **On the basis of a minimum of ten test strips, the tensile energy absorption differential between treated and untreated strips shall not average less than 10% after 28 days of accelerated aging and shall not show a significant increase in Youngs Modulus.**

D. Tensile Analysis After One Defined Fold

An attempt to uncover a testing protocol which would correlate with paper usability is the subject of the attached article. In it, it was discovered that the evaluation of tensile strength after one defined fold is useful in assessing the usability of paper for library purposes.

The tensile strength after one defined fold is done in accordance with TAPPI Test T-494 with one exception. Prior to placing the sample in the jaws of the Instron, it is first folded as described in the attached paper with the device specified. The evaluation is then conducted, and it is noted whether or not the breakage occurred at the resulting fold. All other data are reported as described above. Treated paper shall have a statistically significant average value of at least 10% over the average value of untreated paper.

T 511 om-83
SUGGESTED METHOD—1969
OFFICIAL TEST METHOD—1983
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Folding endurance of paper (MIT tester)

1. Scope

1.1 This method describes the use of the MIT-type apparatus for the determination of the folding endurance of paper. An exhaust fan arrangement maintains the folding head at room temperature.

1.2 The MIT tester is suitable for papers of any thickness; however, if the outer fibrous layers of paper thicker than about 0.25 mm (0.01 in.) rupture during the first few folds, the test loses its significance.

1.3 The procedure for the Schopper-type apparatus is given in TAPPI T 423 "Folding Endurance of Paper (Schopper-Type Tester)."

2. Significance

2.1 Folding endurance tests have been used to estimate the ability of paper to withstand repeated bending, folding, and creasing.

2.2 Folding endurance has also been useful for measuring the deterioration of paper upon aging.

3. Definitions

Folding endurance, the logarithm (to the base 10) of the number of double folds required to break the paper when a strip of paper 15 mm (0.59 in.) wide is tested under a standard tension of 9.81 N (1 kg).

4. Apparatus

4.1 *Folding tester*[1], consisting of:

4.1.1 A spring-loaded clamping jaw constrained to move without rotation in a direction perpendicular to the axis of rotation of the folding head specified below and having its clamping surfaces in the plane of this axis. The load is applied by a spring attached to the jaw assembly which is easily adjustable to provide any desired tension on the specimen within the range of 4.9–14.72 N (500–1500 g). The deflection of the spring when loaded shall be at least 17 mm (0.67 in.) per 9.81 N, which is achieved by using a weight of 1 kg mass.

4.1.2 An oscillating folding head supporting two smooth, cylindrical folding surfaces parallel to, and symmetrically placed with respect to, the axis of rotation. Each of the two folding surfaces shall have a radius of curvature of 0.38 ± 0.015 mm (0.015 ± 0.001 in.) and a width of 19 ± 1 mm (0.75 ± 0.04 in.). The distance separating the folding surfaces is greater than the uncompressed thickness of the paper being tested by no more than 0.25 mm (0.010 in.). The position of the axis of rotation is midway between the common tangent planes of the two folding surfaces. The folding head is provided with a clamping jaw with its nearest edge not less than 9.5 mm (0.375 in.) beyond the axis of rotation. The rotary oscillating movement of the head is such as to fold the paper through an angle of 135° ± 2°, both to the right and to the left of the position of the unfolded specimen.

4.1.3 Various size folding heads are required for testing different thickness of paper. Heads available will accommodate thicknesses from 0 to 0.25 mm (0 to 0.01 in.), 0.25 to 0.50 mm (0.01 to 0.02 in.), 0.50 to 0.75 mm (0.02 to 0.03 in.), 0.75 to 1.02 mm (0.03 to 0.04 in.), 1.02 to 1.25 mm (0.04 to 0.05 in.).

4.2 *Power driven device*, for imparting a rotary oscillating motion of 175 ± 25 cycles/min to the folding clamp.

4.3 *Counter*, for registering the number of double folds required to break the specimen and a device to stop the instrument when the specimen breaks.

4.4 *Strip cutter*, to cut 15-mm-wide parallel strips within ±0.02 mm with clean edges.

4.5 *Exhaust fan*, centrifugal, mounted so that its inlet, not less than 50 mm in diameter, is next to the oscillating head and the specimen being treated, thus drawing the conditioned room air rapidly over both

[1] See separate TAPPI list of suppliers of testing equipment and materials available for this method.

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specimen and head. Its capacity should be great enough to prevent the temperature of the head from rising more than 0.05°C, which can reduce the relative humidity at the fold by about 2% and the number of folds by as much as 10%.

5. Calibration

5.1 The folding test results are very sensitive to tension, arc of fold, and radius of fold; therefore it is essential that regular calibration routines be established and followed.

5.2 Make sure that the folding edges are free from rust, nicks, dirt, and oil and that the counter operates properly.

5.2.1 Measure the plunger friction by determining the additional load required to move the plunger perceptibly under a load of 9.81 N or the load tension used for the testing. This shall not be greater than 0.245 N (25 g).

5.3 The change in tension due to the eccentricity of rotation of the folding edges is measured as follows: Place a test specimen of strong paper of the proper thickness, cut in the machine direction, in the tester as for making a folding test, and apply a tension of 9.81 N or that to be used for the testing. Rotate the folding head slowly by hand throughout the entire folding cycle and measure the maximum change in displacement of the plunger with an accuracy of 0.1 mm (0.004 in.). This displacement shall not be greater than that produced by adding a weight of 35 g (equivalent to 0.343 N).

NOTE 1: The displacement must be equally centered around the plunger position when the strip of paper is straight and the tension is 9.81 N, i.e., when the slot in the folding head is vertical.

5.4 The curvature of the folding edges can be measured by making casts, magnifying them in profile, and comparing them to true circles.

5.5 The two folding edges shall be at the same elevation when the slot head is vertical.

6. Test specimen

Obtain a sample of the paper to be tested in accordance with TAPPI T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, and Related Products." From each test unit of the paper obtain not less than 10 representative specimens in each principal direction of the paper cut accurately to a width of 15 ± 0.02 mm and a length of not less than 130 mm. A 150-mm or longer strip is preferable to provide easier insertion in the clamps. Select specimens that are free from wrinkles or blemishes not inherent in the paper and make sure that the area where the folding is to take place does not contain any portion of a watermark and appears to be of average opacity. The long edges shall be clean cut and parallel.

7. Conditioning

Condition and test the paper in an atmosphere in accordance with TAPPI T 402 "Standard Conditioning and Testing Atmospheres for Paper, Board, Pulp Handsheets and Related Products."

8. Procedure

8.1 Turn the oscillating folding head so that the opening is vertical. Place a 1-kg weight on the top of the plunger (equivalent to the tension desired on the specimen); tap the plunger sideways to minimize friction effects and lock it in position. Without touching the part of the strip to be folded, clamp the specimen lying wholly within one plane, i.e., flat, and with the sides not touching the oscillating jaw-mounting-plate. Remove the weight and unscrew the plunger lock to apply the specified tension to the test strip. If the reading of the load indicator changes, reclamp the specimen to give it its proper tension. Whenever possible, use a tension of 9.81 N (1 kg), but if this gives an unreasonably high or low test result, use more or less tension: 14.72 N or 4.9 N (1.5 or 0.5 kg).

NOTE 2: The number of the folds may vary by as much as the cube of the applied tension.

8.2 Set the counter to zero and place the centrifugal fan so that its inlet is almost touching and is across the specimen and oscillating head. Start the fan and the instrument motor. Fold the strip at a uniform rate of 175 ± 25 double folds per minute until it breaks. Record the number of double folds made before fracture. If there is any appreciable delay between tests on successive specimens, keep the fan running to prevent the head warming by conduction from its shaft.

NOTE 3: Whenever practicable, use a tension of 9.81 N; however, if this does not give satisfactory results, use more or less tension and state the actual tension used in a prominent position in the report.

9. Report

9.1 For each test unit record the number of double folds for the machine and cross directions. Convert the raw data to the logarithm (base 10) by using common log tables. Calculate the mean of the logs and report as $\log_{10}$ MIT folding endurance to two significant figures. State clearly if a tension other than 9.81 N (1 kg) was used. Include the number of specimens tested, and the maximum and minimum $\log_{10}$ of the fold number obtained in each direction.

9.2 *Alternate report permitted.* Although the preferred method for reporting MIT folding endurance is that in 9.1, an alternate procedure of reporting the number of double folds for the machine and cross directions of the paper separately is permitted.

9.3 Tests made on strips having their length in the machine direction are designated as being the "machine direction," and similarly for the cross direction.

10. Precision

10.1 Repeatability (within a laboratory) = 0.12 $\log_{10}$ fold or 5.8% for number of double folds.

10.2 Reproducibility (between laboratories) = 0.39 $\log_{10}$ fold or 18.7% for number of double folds, in accordance with the definitions of these terms in TAPPI T 1206 "Precision Statement for Test Methods."

10.3 The above precision is calculated from data taken from 36 reports of the TAPPI Collaborative Reference program for paper.

NOTE 4: This method is very susceptible to small errors in adjustment and calibration of the instrument and in the relative humidity of the test room. Limits as much as two times those shown may be expected if the instructions are not followed meticulously (*1-6*).

11. Additional information

11.1 Effective date of issue: February 15, 1983.

11.2 This revision consists of the following: The definition of the folding endurance is revised to reflect the reporting of the results as the $\log_{10}$ of the number of double folds required to break the specimen under the test conditions. The report is changed to permit the results to be reported as the $\log_{10}$ MIT folding endurance or number of double folds. The method is also put into current format for TAPPI Test Methods.

11.3 The rationale for reporting the $\log_{10}$ fold is as follows:

11.3.1 The greatest source of test variability is that the folding stresses are applied to a very small area of paper. Failure occurs at this point and not, as in normal tensile test, at the weakest point in the test strip. Thus, "within-sample" variability is great. In addition, the fold test operates cumulatively, the reduction in strength at the test point being approximately exponential. Therefore, it is possible for two test pieces of similar initial tensile strength at the test points and with identical rates of loss of strength with folding to give very different folding numbers. It is thus unfortunate that the number of double folds has been used to represent folding endurance. A suitable fractional power of the fold number or the $\log_{10}$ of the fold number provides a much more realistic and less misleading result.

11.3.2 Naoumof (*1*) (as early as 1905), Korn (*3*), and Krohnstad (*7*) all have used the log of the fold number in evaluating the significance of folding endurance results. Van Nederveen and Van Royen (*5*) and Andersson (*6*) both consider that the log of the fold number is a better measure of folding endurance than the fold number itself, and Brecht and Wesp (*8*) generally supported this view.

11.4 The reporting of the log fold is supported by ISO/TC6/SC2/W5 (Secretariat-2) June 8, 1968 and ISO 5626 dated December 15, 1978.

11.5 Related methods: ASTM 2176; Canadian CPPA D17; Australian APPITA 423; British BSI 4419.

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Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Test Methods Administrator. ■

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OFFICIAL STANDARD – 1926
TENTATIVE STANDARD – 1964
OFFICIAL TEST METHOD – 1982
REVISED – 1988
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Internal tearing resistance of paper (Elmendorf-type method)

1. Scope

1.1 This method measures the force perpendicular to the plane of the paper required to tear multiple sheets of paper through a specified distance after the tear has been started using an Elmendorf-type tearing tester. The measured results can be used to calculate the approximate tearing resistance of a single sheet. In the case of tearing a single sheet of paper, the tearing resistance is measured directly.

1.2 It is not suitable for determining the cross-directional tearing resistance of highly directional boards and papers. These materials are covered by TAPPI T 496 "Cross Directional Internal Tearing Resistance of Paperboard."

1.3 For edge-tear resistance see TAPPI T 470 "Edge Tearing Resistance of Paper (Finch Method)."

2. Summary

One or more sheets of the sample material are torn together through a fixed distance by means of the pendulum of an Elmendorf-type tearing tester. The work done in tearing is measured by the loss in potential energy of the pendulum. The instrument scale is calibrated to indicate the average force exerted when a certain number of plies are torn together (work done divided by the total distance torn).

3. Significant test variables

3.1 Several Elmendorf-type tearing testers are available and in use throughout the world, principally those of Australian, British, German, Swedish, and United States manufacture. In addition, testing practices also vary, as is reflected in the related methods for these countries or others listed in 10.3. Instruments and practices in use vary in at least three major respects:

3.1.1 One difference is in the design of the pendulum sector. The oldest model without deep cutout permitted the specimen to come in contact with the sector during the test and gave values significantly higher than those obtained using the newer models *with* a deep cutout (see Fig. 1) which eliminate this undesirable friction. The magnitude of the difference in value obtained using different styles of the instrument de-

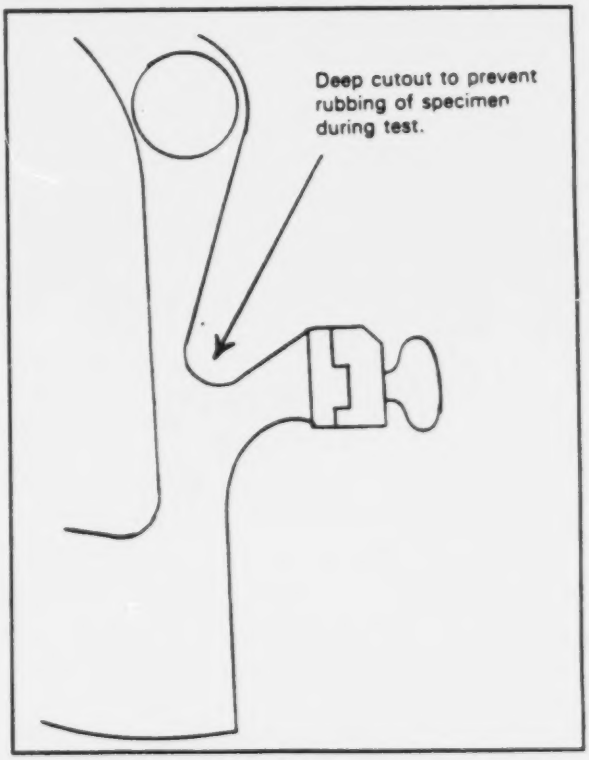

Fig. 1. Newer testing model with deep cutout.

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52

scribed in this test method varies as a function of instrument and with different types and grammages of paper. The instrument having the oldest-style sector does not meet the requirements of this test method. With a few materials, test values have been observed (*1*) to be as much as 10% greater with the oldest-style sector.

3.1.2 The second difference is in the design of the specimen clamps which, together with the structural characteristics of the paper which govern the nature of the tear with respect to its splitting tendencies during the test, can have an appreciable influence on the mode of tearing and may result in significant differences (*2*). The procedure described in Section 7.3 reduces this effect. The clamp designs used by some manufacturers may vary even for their own models. Instruments are available with pneumatically activated grips as well. When available, their use minimizes variations due to differences in clamping pressures exerted by manually tightened grips.

3.1.3 The third difference results from a combined variation in testers and testing practices. As measured tearing resistance increases or decreases for different types of paper, it may become so large or so small as to be outside the practical range of the instrument. This problem may be overcome in one of two ways; the number of sample sheets tested at one time may be changed, or the mass of the instrument pendulum may be changed either by addition of augmenting weights or by replacement of the entire pendulum with one of a different known mass. The tearing length must never be varied in an effort to alter the pendulum capacity.

3.2 The foregoing, together with other lesser differences in design details between instruments or testing practices, preclude specifying a tearing instrument and method that would give essentially the same test results when using Elmendorf instruments of different design and manufacture. Even for one specific model, some procedural variables such as the number of plies torn may alter the test values calculated on a single sheet basis substantially. Hence, by necessity, this reference method must be arbitrary and is limited to the described procedure used with instruments conforming to all of the requirements specified under Section 4.

4. Apparatus

4.1 Elmendorf tearing tester (*3–5*), with a cut-out as shown in Fig. 1, which prevents the specimen from coming in contact with the pendulum sector during the test, and having the following elements:

4.1.1 A stationary clamp; a movable clamp carried on a pendulum formed by a sector of a circle free to swing on a ball bearing; a knife mounted on a stationary post for starting the tear; means for leveling the instrument; means for holding the pendulum in a raised position and for releasing it instantaneously; and means for registering the maximum arc through which the pendulum swings when released.

4.1.1.1 The registering means may consist of a graduated scale mounted on the pendulum, a pointer mounted on the same axis as the pendulum with constant friction just sufficient to stop the pointer at the highest point reached by the swing of the sector, and an adjustable pointer stop for setting the zero of the instrument.

4.1.1.2 The pointer and scale may be replaced by a digital readout unit which gives readings of equivalent accuracy and precision (*6*).

4.1.2 With the pendulum in its initial position ready for a test, the clamps are separated by an interval of 2.8 ± 0.3 mm and are so aligned that the specimen clamped in them lies in a plane parallel to the axis of the pendulum, the plane making an angle of 27.5 ± 0.5° with the perpendicular line joining the axis and the horizontal line formed by the top edges of the clamping jaws. The distance between the axis and the top edges of the clamping jaws is 103.0 ± 0.1 mm. The clamping surface in each jaw is at least 25 mm wide and 15.9 ± 0.1 mm deep.

NOTE 1: In the past, it has been the practice for instruments commonly available in the United States to be equipped with 36 ± 1 mm wide jaws. Instruments currently available, however, may be equipped with jaws as narrow as 25 mm. Testing has shown that the effect of jaw width on test results is statistically insignificant. It is recommended, however, that the test specimen length be adjusted to match jaw width. See Note 6.

4.1.3 The instrument measures the energy (work done) used by the pendulum in tearing the test specimen. In order to convert to average tearing force, the energy must be divided by the total distance through which the force is applied. This division may be accomplished by the electronics in digital read-out instruments so that the read-out is directly in grams-force or in millinewtons (SI unit of force). For pointer and scale instruments, the scale may be in millinewtons or in grams-force for a specified number of plies; i.e., when the specified number of plies are torn together, the scale reading gives the average tearing resistance (force) of a single ply.

4.1.4 Instruments of several capacities e.g., about 2000, 4000, 8000, 16,000, 32,000 mN (200, 400, 800, 1600, 3200 gf) and perhaps others are available, with the several capacities being achieved by individual instruments, interchangeable pendulum sectors, or augmenting weights. The instrument recognized as "standard" for this method has a capacity of 1600 gf (SI equivalent 15.7 N); i.e., it has a pendulum sector of such mass and mass distribution that its 0 to 100 scale is direct reading in grams-force per ply when 16 plies are torn together. For a 16-ply test specimen, the tearing distance K = 16 x 4.3 cm (tearing distance per ply) x 2 = 137.6 cm, the factor 2 being included since in tearing a given length the force is applied twice the distance. Likewise, for a 16-ply test specimen, the tearing energy per ply for a scale reading of 100 would then be 100 gf x 137.6 cm or 13760 gf cm (SI equivalent 1349.4 mJ). For some of the instruments of different capacities where different numbers of plies are required, or when the number of plies tested using the "standard" instrument differs from 16, different values of K and/or the tearing energy per ply may be calculated, using the above calculation as a model.

4.1.5 In the "standard" instrument, the zero reading on the scale is at about 70° from the center line (i.e., the vertical balance line when the pendulum hangs freely), the 100 reading is at about 21° from the center line, and a vertical force of 1057.3 ± 2.0 gf (SI equivalent 10.369 ± 0.020 N) applied at 22.000 ± 0.005 cm from the pendulum axis is required to hold the pendulum sector at 90° from its freely hanging position. Other tearing instruments will require vertical forces that are factors of 2 greater or smaller than 1057.3 gf and, if calibrated in millinewtons, the zero reading would remain at 70° and the 1000 reading would be at about 19° (or the 981 reading at about 21°).

4.1.6 The cutting knife for the test specimen is centered between the clamps and adjusted in height so that the tearing distance is 43.0 ± 0.2 mm; i.e., the distance between the end of the slit made by the knife and the upper edge of the specimen is 43.0 ± 0.2 mm when the lower edge of the 63.0-mm wide specimen rests against the bottom of the clamp.

4.2 *Specimen cutter*, to insure parallel specimens 63.0 ± 0.15-mm wide with sharp and clean edges. For this purpose it is desirable to use the type having two hardened and ground base shears, twin knives tensioned against the base shears, and a hold-down mechanism.

5. Calibration and adjustment

5.1 *Verification of scale*

5.1.1 Once the scale has been verified, it is unnecessary to repeat this step, provided the tester is kept in adjustment and no parts become changed or perceptibly worn. The scale may be verified either by the potential energy method or by the method which uses the check weights obtainable from the manufacturer. The potential energy method is relatively time-consuming and complicated. The check weight method is relatively simple.

5.1.2 *Potential energy method.* The procedure (*7*) for verification is as follows: Anchor and level the tester as later described. Clamp a known weight (in grams) W to the radial edge of the sector beneath the jaws, the center of gravity of the weight (including means of attaching) having been previously marked by a punched dot on the face of the weight that is to be toward the front of the instrument. Close the jaw of the clamp in the sector. Raise and set the sector as for tearing a sheet and, by means of a surface gauge or cathetometer, measure in centimeters, to the nearest 0.01 cm, the height H of the center of gravity of the weight above a fixed horizontal surface. Then release the sector, allow it to swing and note the pointer reading. Without touching the pointer, raise the sector until the edge of the pointer just meets with its stop, in which position again determine the height h of the center of gravity of the weight above the fixed surface.

5.1.2.1 The work done is $W(h-H)$ gf cm. For the standard 1600 gf tester, the pointer reading should be $W(h-H)/K$, where K = 137.6 cm. For other instruments graduated for grams-force of greater or lesser capacity, the reading will be factors of 2 greater or smaller. If graduated for millinewtons, the additional factor 9.81 must be applied.

5.1.2.2 One or more weights may be clamped on the edge of the sector for each calibration point, the work done in raising each weight being calculated and added together.

5.1.2.3 If the deviations of the indicated readings are greater than one-half division, the instrument should be returned to the manufacturer for repair and adjustment.

5.1.2.4 Calibration weights may or may not be available from the manufacturer of the instrument for use in calibration.

5.1.3 *Verification of Scale – Check Weight Method.* Use Check Weights calibrated for suitable scale values (i.e., 20%, 50% and 80% of pendulum capacity.) Different Check Weights are needed for each pendulum capacity. These weights should be so constructed that each weight can be inserted in the clamps by the procedure used for a test specimen.

5.1.3.1 With the pendulum in the raised position, open the clamp of the pendulum. Slide the weight into position and fasten it securely into the clamp. The body of the weight must be beneath the clamp. Depress the pendulum stop, thus releasing the pendulum. Hold down the stop until after the pendulum swing is completed, and catch the pendulum on the return swing. Read the indicating device to the nearest division.

5.1.3.2 Repeat this procedure with each of the check weights.

5.2 *Adjustment of tearing distance*

5.2.1 To check the 43.0-mm tearing distance, apply a small amount of graphite (from an ordinary pencil), to the cutting knife so that when the cut is made, some of the graphite transfers to the paper. This serves to contrast the cut from the uncut portion of the paper and facilitates the measurement. Make this measurement with a vernier caliper with a depth gauge or a good quality steel rule, readable to 0.2 mm or better under magnification. An alternative procedure is to use a go, no-go gauge, which may be available from the manufacturer of the instrument.

5.3 *Adjustment of instrument for operation*

5.3.1 *Pendulum notching.* Sometimes, as a result of frequent use, a notch is worn in the pendulum sector at the point of contact with the sector stop, giving a jerky release of the pendulum. If this happens, either repair the sector by cutting out and replacing the worn edge, or adjust the height of the stop to the very lowest point of the sector edge. In this case, recheck the calibration of the scale.

5.3.2 *Clamp alignment and knife condition.* Rest the pendulum sector against its stop, and check the alignment of the clamps. Adjust the pendulum stop if necessary. Verify by visual check that the knife is centered between the clamps, and adjust if necessary. Check the sharpness of the knife. A dull knife will result in a square notch near the top of the cut with the paper pushed out. If necessary, sharpen the knife with a rough stone; a rough edge is better than a sharp, smooth edge. Check the tearing distance and adjust the height of the knife if necessary. *Do not* change the dimensions of the specimen to adjust the tearing distance.

5.3.3 *Instrument mounting.* Support the instrument on a table so rigid that there will be no perceptible movement of the table or instrument during the swing of the pendulum. Any

movement of the instrument base during the swinging of the pendulum may be a significant source of error.

NOTE 2: Threaded bolt holes are usually provided in the base of the instrument and may be used to secure the instrument to the table. An alternative procedure is to place the instrument on a guide which ensures that the instrument always has the same position on the table. Such a guide may be available from the manufacturer of the instrument.

5.3.4 *Instrument leveling.* Level the instrument so that, with the sector free, the line on the sector indicating the vertical from the point of suspension is bisected by the edge of the pendulum stop mechanism.

5.3.5 *Pendulum friction (older instruments).* Draw a pencil line on the stop-mechanism 25 mm to the right of the edge of the sector stop. Raise the sector to its initial position and set the pointer against its stop. On releasing the sector and holding the sector stop down, the sector should make at least 20 complete oscillations before the edge of the section which engages the stop no longer passes to the left of the pencil line. Otherwise, clean, oil, and adjust the bearing.

5.3.6 *Pendulum friction (newer instruments).* In recent years, a new type of frictionless bearing made of synthetic material has been used. This bearing will not necessarily allow the pendulum sector to make 20 complete oscillations as the older one did. This does not mean that there is excess friction in the pendulum swing. These newer bearings should not be oiled. Consult the instructions supplied with the instrument for guidance.

5.3.7 *Pointer zero reading.* Operate the leveled instrument several times with nothing in the jaws, the movable jaw being closed. If zero is not registered, the pointer stop should be adjusted until the zero reading is obtained. Do not change the level to adjust the zero.

5.3.8 *Pointer friction.* Set the pointer at the zero reading on the scale before releasing the sector, and after release see that the pointer is pushed not less than 2.5 mm nor more than 4.0 mm beyond the zero. If the pointer friction does not cause it to lie between these two distances, remove the pointer, wipe the bearing clean, and apply a trace of good clock oil to the groove of the bearing, adjust the spring tension or make other adjustments to achieve the specified friction. Reassemble, readjust the zero setting, and recheck the pointer friction.

6. Sampling and test specimens

6.1 Sample the paper in accordance with T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Product." From each test unit of the sample, prepare 10 representative specimens in each principal direction of the paper, unless a test in only one direction is required. For each specimen keep the wire sides of all the plies facing the same way.

NOTE 3: It has been found (*8*) that there is usually no advantage in testing more than 10 specimens of a homogeneous test unit of the sample.

6.2 Cut each ply for a test specimen at least 53 mm long by 63.0 ± 0.15 mm wide, taking all the plies to be torn together from a single sheet, or if this does not provide sufficient material, from adjacent sheets of a unit.

NOTE 4: The correct length of the test specimen to be used in making a test, measured in millimeters, is equal to the distance between the outermost edges of each of the instrument's jaws (± 2 mm). For the instrument described in 4.1.2, that distance is at least 2 x 25 mm (the minimum width for each jaw face) plus 2.8 mm (the distance between the clamps) or at least 53 mm. In the United States, the majority of instruments have jaws 36 ± 1 mm wide. In such cases, a test specimen length of 76 ± 2.0 mm, specified in previous versions of this method, continues to be the correct length.

6.3 Determine from a preliminary test or the product specification how many plies are needed to make up a specimen so that, when torn together on the instrument having a 15.7-N (1600-gf) capacity, they give an instrument scale reading nearest 40% of full scale.

NOTE 5: The work done in tearing a number of sheets of paper includes a certain amount of work to bend the paper continuously as it is torn to provide for the rubbing of the torn edges of the specimen together and to lift the paper. The number of plies torn at one time and their size can affect the test result with some papers. Empirical requirements for both the apparatus and the method are therefore necessary to keep the additional work not used for tearing to a definite quantity. For this reason, in making comparisons between two or more sets of paper of the same type and grammage, use the same number of plies for each set.

6.4 If a single-ply test specimen gives a reading higher than 75 on the standard 1600 gf instrument (75% of full scale on other instruments), use the next higher capacity instruments with one ply or, if necessary, a still higher capacity instrument.

NOTE 6: For weaker papers, the standard 1600-gf instrument may require that 16 or more plies be torn together under the procedure specified in 6.3. For these papers, and provided lower capacity instruments are available, the number of plies may be restricted to four and the next lower capacity instrument may be used whenever the reading falls below 20% of full scale. The ISO 1974 procedure provides for testing four-ply specimens with multiple pendulum instruments. If this alternative procedure is used, so state in the report.

7. Procedure

7.1 Precondition, condition, and test the specimens in accordance with T 402 "Standard Conditioning and Testing Atmospheres for Paper, Board, Pulp Handsheets, and Related Products."

7.2 Raise the pendulum sector to its initial position and set the pointer against its stop. Center the specimen in the clamps with the bottom edge carefully set against the stops. Securely clamp the specimen using approximately the same pressure on both clamps. Make the initial slit. Depress the pendulum stop quickly as far as it will go to release the pendulum. Hold down the stop until after the tear is completed and catch the pendulum on the return swing without disturbing the position of the pointer.

7.3 Make only one test per specimen, each specimen consisting of the same number of plies. Make tests alternately with the wire sides of all the plies of a specimen facing the pendulum and with the wire sides of all the plies away from the pendulum. Make certain that the specimen leans toward and not away from the pendulum by gently creasing the specimen at the clamp if necessary, but in doing so avoid affecting the relative humidity of the test area (9).

7.4 Record the scale readings to the nearest half division; also record the number of plies used in the specimens.

7.5 If the line of tear fails to pass through the top edge of the specimen but deviates to one side, note and report this, but do not use the reading so obtained. If more than one-third of the tests exhibit this behavior, this method should not be used for the material concerned. If the sheets split extensively when being torn, this also should be reported.

7.6 Calculate the average tearing force in millinewtons and, if desired, in grams-force required to tear a single ply as follows:

7.6.1 If the standard 1600-gf instrument with 0-100 scale is used:

Average tearing force, mN = (16 x 9.81 x average scale reading) / number of plies

Average tearing force, gf = (16 x average scale reading) / number of piles

7.6.2 If an instrument of different grams-force capacity with 0–100 scale is used:

Average tearing force, mN =
(16 x 9.81 x avg. scale reading x gf-capacity) / (number of plies x 1600 gf)

Average tearing force, gf =
(16 x average scale reading x gf-capacity) / (number of plies x 1600 gf)

7.6.3 If an instrument has an SI metric scale (e.g., 0–1000 graduations):

Average tearing force, mN =
(16 x avg. scale reading x capacity, N) / (number of plies x 15.7 N)

Average tearing force, gf =
(16 x avg. scale reading x capacity, N) / (9.81 x number of plies x 15.7 N)

7.6.4 If an instrument has a direct-reading scale (e.g., digital read-out) that directly gives the force per ply when preset for the number of plies:

Average tearing force, mN = scale reading if directly in millinewtons, *or*
= 9.81 x scale reading if in grams-force

Average tearing force, gf = scale reading / 9.81, if scale is in millinewtons, *or*
= scale reading if directly in grams-force

NOTE 7: Previously, a standard reference material (NBS Standard Sample No. 704) was available for use with this method (*10*). Instructions accompanying the material described a procedure to correct values when using this standard. Currently, this standard reference material has been exhausted and will not be replaced.

8. Report

8.1 Report results with the tear parallel with the machine direction as resistance to internal tearing in the machine direction and those with the tear perpendicular to the machine direction as resistance to internal tearing in the cross direction.

8.2 For each principal direction, report the average, maximum, and minimum of accepted test values of the force required to tear a single ply to three significant figures.

8.3 For a complete report, state the number of plies torn at one time; the number and value of any rejected readings and reasons for their rejection; if an augmenting weight was used; and the make and model number of the instrument used.

9. Precision

9.1 On the basis of studies made in accordance with T 1200 "Interlaboratory Evaluation of Test Methods Used with Paper and Board Products," the precision of test results representing the average of ten readings, has been found to be as follows:

9.1.1 Repeatability (within a laboratory) = 4.2%

9.1.2 Reproducibility (between laboratories) = 12.5%

9.1.3 Comparability (between materials) = 6.9%, in accordance with the definition of these terms in T 1206 "Precision Statement for Test Methods." Previously, reproducibility could be reduced to 8.3% by using a reference material for standardizing the instruments; however, this material is no longer available (see Note 7).

9.2 In each of the above situations, two test results, each representing an average of ten readings, may be considered alike with a probability of 95% when the two results agree within the appropriate value shown above.

10. Additional information

10.1 Effective date of issue: November 30, 1987.

10.2 The principal changes made in this revision are: (a) discussion of the check weight method of scale verification; and (b) inclusion of the discussion on the new type of pendulum bearings.

10.3 Related methods: ASTM, D 689; Australian Appita, P400; British BS 4468; Canadian CPPA, D.9; ISO 1974; SCAN-P 11:73.

10.4 Other references related to this method are by Jones and Galley (*11*), Van den Akker, Wink, and Van Eperen (*12*), Sun, Wilson, and Bach (*13*), Lashof (*14*), and Swartout and Setterholm (*15*).

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Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Technical Divisions Administrator. ■

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REVISED – 1978
OFFICIAL TEST METHOD – 1986
REVISED – 1989
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Edge tearing resistance of paper (edge-tear stirrup method)

1. Scope

1.1 This method describes a procedure for determining the edge tearing strength of paper. A strip of paper is simultaneously torn at opposite points at the edges of the strip by means of a thin V-notched beam held in a stirrup which is fastened in one of the clamps of a tensile testing machine.

1.2 The use of this test is limited to papers which will fold evenly (no breaks or fracturing) over the V-notched beam.

2. Significance

When paper is subjected to high stresses on handling equipment, good edge-tearing resistance is very important. The force necessary to start a tear is greater than the internal tear as measured in TAPPI T 414 "Internal Tearing Resistance of Paper." Although the forces are related, testing for both types of tears is important.

3. Apparatus

3.1 *Edge-tear stirrup*[1] (Fig. 1), attached to a tensile testing machine. The edge-tear stirrup consists of a thin steel plate which forms a horizontal beam supported on edge by the ends of a stirrup-shaped frame. The thin metal tang of the stirrup frame is fastened in the lower clamp of the tensile testing machine, so that the vertical center line of the stirrup coincides with the line connecting the midpoints of the upper and lower clamps. The horizontal beam is removable from the stirrup frame, and two beams of different thicknesses are furnished for use with papers of different thickness ranges. The beam thickness is to be selected with reference to the paper thickness as follows:

Paper thickness	*Beam thickness*
0.76 mm (0.030 in.) and under	1.27 ± 0.05 mm (0.050 ± 0.002 in.)
Over 0.76 mm (0.030 in.)	2.54 ± 0.05 mm (0.100 ± 0.002 in.)

The edge of the beam forms a shallow V-notch, the sides of which subtend an angle of 150 ± 1°. The sides of the V-notch are semicircular in cross-section. They are formed either by filing and scraping with a semicircular-shaped scraper or by soldering a drill rod (of a diameter equal to the thickness of the beam) to the edges of the V-notch. In either case the edges of the V-notch are required to be smooth, straight, and semicircular in cross section. Test results are highly sensitive to any deviations from these requirements.

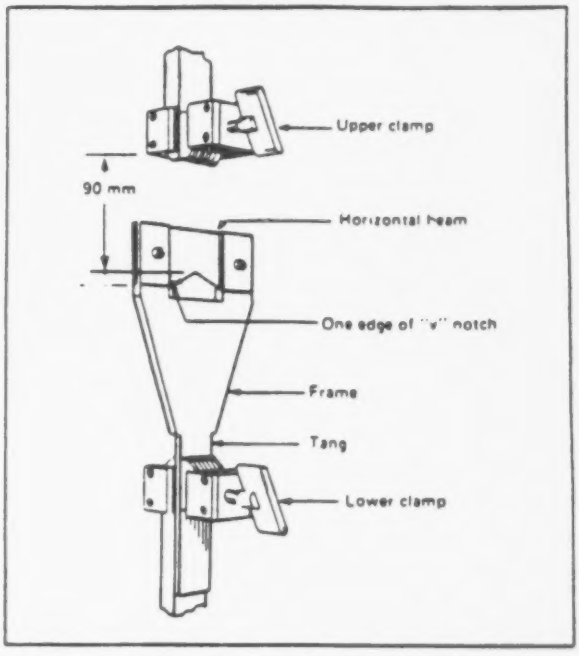

Fig. 1. Fixture separation prior to specimen insertion.

[1]Names of suppliers of testing equipment and materials for this method may be available from the TAPPI Information Resources Center.

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3.2 *Sample cutter*, a precision sample cutter capable of cutting a specimen 15.0 ±0.1 mm wide by at least 250 mm long.

3.3 *Tensile testing machine*. The tensile testing machine shall conform to the requirements of TAPPI T 494 "Tensile Breaking Properties of Paper and Paperboard (Using Constant Rate of Elongation Apparatus)."

4. Sampling and test specimens

4.1 Obtain a sample of the paper in accordance with TAPPI T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Product."

4.2 From each test unit cut 10 specimens in each principal direction 15 mm wide and approximately but not less than 250 mm long. The edges must be parallel and clean cut. Any nicked or ragged edge might cause an erroneous result.

5. Procedure

5.1 Condition the specimens in an atmosphere in accordance with TAPPI T 402 "Standard Conditioning and Testing Atmospheres for Paper, Board, Pulp Handsheets, and Related Products."

5.2 Attach a beam of the proper thickness to the stirrup frame.

5.3 Fasten the tang of the stirrup in the lower clamp of the tensile testing machine so that the vertical center line of the stirrup coincides with the line connecting the midpoints of the upper and lower clamps of the testing machine. Ensure that the sides of the V-notch are symmetrically located with the line through the midpoints of the clamps.

5.4 Place the clamps of the machine so that the lower edge of the upper clamp is 90 ± 1 mm (3.5 ± 0.04 in.) above the vertex of the V-notch.

NOTE 1: If a line-contact upper jaw is used then the span of 90 ± 1 mm should be measured from the top of the V-notch to the line contact of the top jaw.

5.5 Thread the test specimen through the stirrup, under the beam, and bring the two ends together and fasten them in the upper clamp as shown in Fig. 2. In this operation, most of the slack in the specimen is taken up, but care should be exercised not to apply sufficient stress to start tearing the specimen.

5.6 Apply a tearing force to the specimen at a constant rate of elongation of 25 ± 5 mm/min (1.0 ± 0.2 in./min). The initial force applied by hand should have the strip taut with no force indicated. This procedure allows the force to be uniformly distributed.

5.7 Record the maximum load required to start tear.

6. Report

6.1 Report the average and standard deviation in Newtons for each principal direction of the paper to two significant figures. The conversion factors are: 1 lbf = 4.448 N; 1 kgf = 9.807 N.

6.2 Report the thickness of beam used, rate of elongation, width, and thickness of test specimens.

6.3 The edge tearing, cross direction, is the result obtained on strips cut in the machine direction, and the machine direction result is from those strips cut in the cross direction.

7. Precision

7.1 Repeatability (within a laboratory) = 5.0%.
7.2 Reproducibility (between laboratories) = not known.
7.3 Comparability = not known.

8. Additional information

8.1 Effective date of issue: December 15, 1989.

8.2 This method was revised in 1947, became an Official Standard in 1954, corrected in 1966, and revised again in 1978. Report of results has been changed to SI system of units.

8.3 Related method: Canadian CPPA D26P "Edge Tearing Strength of Paper (Finch Method)."

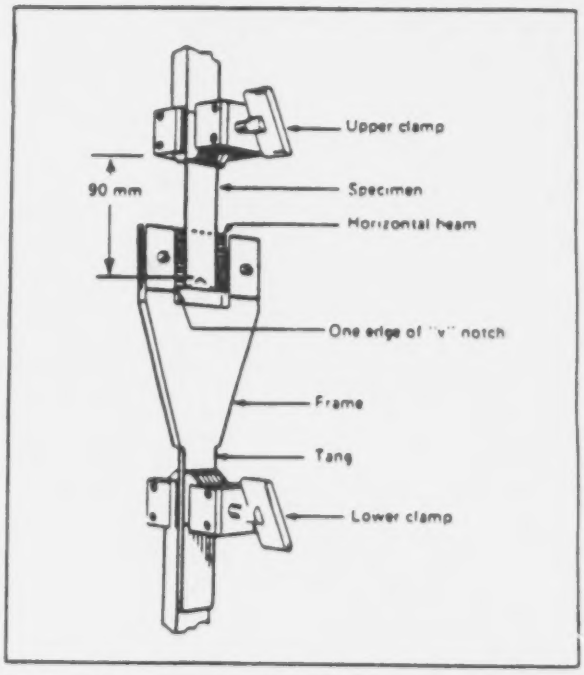

Fig. 2. Fixture separation after specimen insertion (V-notch indicated by dotted lines).

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Technical Divisions Administrator. ■

T 494 om-88
SUGGESTED METHOD — 1964
OFFICIAL STANDARD — 1970
OFFICIAL TEST METHOD — 1981
CORRECTED — 1982
REVISED — 1988
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Tensile breaking properties of paper and paperboard (using constant rate of elongation apparatus)

1. Scope

1.1 This test method describes the procedure, using constant-rate-of-elongation equipment, for determining three tensile breaking properties of paper and paperboard, namely: the force per unit width required to break a specimen (tensile strength), the percentage elongation at break (stretch), and the energy absorbed per unit area of the specimen before breaking (tensile energy absorption).

1.2 This procedure is applicable to all types of paper and paperboard within the limitations of the instruments used, whether the instruments perform horizontal or vertical tests or whether they are manually operated or computer controlled. It may be applicable to handsheets as specified in TAPPI T 220 "Physical Testing of Pulp Handsheets." It does not apply to combined corrugated board.

1.3 TAPPI T 404 "Tensile Breaking Strength and Elongation of Paper and Paperboard (Using Pendulum-Type Tester)" describes a procedure for measuring tensile strength and stretch using pendulum-type instruments. T 494 describes the procedures for determining stretch, tensile energy absorption, and tensile strength.

2. Definitions

2.1 *Tensile strength*, the maximum tensile stress developed in a test specimen before rupture on a tensile test carried to rupture under prescribed conditions. Tensile strength (as used here) is the force per unit width of test specimen.

2.2 *Stretch*, the maximum tensile strain developed in the test specimen before rupture in a tensile test carried to rupture under prescribed conditions. The stretch (or percentage elongation) is expressed as a percentage, i.e., one hundred times the ratio of the increase in length of the test specimen to the original test length.

2.3 *Tensile energy absorption* (TEA), the work done when a specimen is stressed to rupture in tension under prescribed conditions as measured by the integral of the tensile stress over the range of tensile strain from zero to maximum strain. The TEA is expressed as energy per unit area (test span x width) of test specimen.

2.4 *Breaking length*, the calculated limiting length of a strip of uniform width, beyond which, if such a strip were suspended by one end, it would break of its own weight.

2.5 *Tensile index*, the tensile strength in N/m divided by grammage.

NOTE 1: ISO/TC6 recommends the use of tensile index over breaking length (2.4). See TIS 0800-01 (old number 018-4) "Units of Measurement and Conversion Factors."

3. Significance

3.1 Tensile strength is indicative of the serviceability of many papers, such as wrapping, bag, gummed tape, and cable wrapping, which are subjected to direct tensile stress. The tensile strength of printing papers is indicative of the potential resistance to web breaking during printing and other converting operations and during travel of the web from the roll through the equipment.

3.2 Stretch (sometimes with bending stiffness) is indicative of the ability of paper to conform to a desired contour. It is important for creped paper, towels, napkins, decorative papers, industrially used paper tapes (both creped and pleated), bags, and liners for cans, barrels, or cartons.

3.3 Tensile energy absorption is a measure of the ability of a paper to absorb energy (at the strain rate of the instrument) and indicates the durability of papers which are subjected to repetitive straining and stressing, such as multiwall sack papers.

4. Apparatus

4.1 *Tensile testing machine*, a constant-rate-of-elongation type (*1*), meeting the following requirements:

4.1.1 Two clamping jaws, each with a line contact for gripping the specimen, with the line of contact perpendicular to the direction of the applied load and with means for controlling and adjusting the clamping pressure.

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NOTE 2: "Line contact" describes the clamping zone resulting from gripping the specimen between a cylindrical and a flat surface or between two cylindrical surfaces whose axes are parallel (2).

NOTE 3: For certain grades of paper "line contact" jaws may not be appropriate and it may be necessary to substitute flat gripping surfaces. Certain grades are damaged by the "line contact" loading between cylindrical and flat surfaces.

4.1.2 The clamping surfaces of the two jaws shall be in the same plane and so aligned that they hold the test specimen in that plane throughout the test.

4.1.3 The distance between line contacts at the start of the test shall be adjustable and resettable to ± 0.5 mm (±0.02 in.) for the specified initial test span (6.4).

4.1.4 The rate of separation of jaws shall be 25 ± 5 mm/min (1.0 ± 0.2 in./min), or as otherwise noted (6.5) and once set shall be resettable and constant to ±4%.

4.1.5 Recorder or indicator should be readable to 0.25% of full scale loading force and capable of retaining a calibration accuracy of ±0.5% of full scale.

4.1.6 Recorder speed or indicator shall be adjustable to provide a readability and accuracy of ±0.05% stretch (that is, ±0.09 mm elongation for a test span of 180 mm).

4.2 *Alignment jig* (optional) (2) to facilitate centering and aligning the specimen in the jaws, so that the clamping lines of contact are perpendicular to the direction of the applied force and the center line (long dimension) of the specimen coincides with the direction of applied force.

4.3 *Planimeter* or *integrator*, respectively, to measure the area beneath the load-elongation curve or to compute directly the work to rupture, with an accuracy of ±1%.

4.4 *Specimen cutter*, for cutting specimens of the required width, with straight parallel sides (5.3).

4.5 *Magnifier and scale* or optical comparator, capable of measuring the specimen width to the nearest 0.1mm (0.004 in.).

NOTE 4: Fully automated laboratory management and/or data acquisition systems are available which perform several functions such as: automatic calibration check, pre-setting and storing a variety of test programs, cutting the test strip, acquiring test data, and accurately determining the tensile breaking properties of paper and paperboard. These tests may be performed with the test strip horizontal or vertical by such equipment. Such equipment may be suitable for use in performing this method; however, the user is responsible for making independent assessment of this fact on the basis of data generated using specific equipment.

5. Sampling and test specimens

5.1 Obtain a sample of the paper in accordance with TAPPI T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Product."

5.2 Precondition, then condition the sample in accordance with TAPPI T 402 "Standard Conditioning and Testing Atmospheres for Paper, Board, Pulp Handsheets, and Related Products" prior to cutting the specimens.

NOTE 5: The exposure of the paper to a high relative humidity before preconditioning and conditioning can lead to erratic results varying from a decrease in stretch and tensile to a substantial increase (30% increase in stretch not uncommon) in these properties. Consequently, TEA is similarly affected. Careful protection of the sample from the time of sampling until testing is therefore very important.

5.3 Cut 10 test specimens from each test unit of the sample in each principal direction of the paper 25 ± 1 mm (0.98 ± 0.04 in.) wide with sides parallel within 0.1 mm (0.004 in.) and long enough to be clamped in the jaws when the test span is 180 ± 5 mm (7.1 ± 0.2 in.), leaving enough length so that any slack can be removed from the strip before clamping. Insure that strips are free from abnormalities, creases, or wrinkles. When the test span is less than 180 ± 5 mm (7.1 ± 0.2 in.), see Appendix A.3.1.2. In some cases, it may be impossible or impractical to obtain a test specimen having a length long enough to be clamped in the jaws having the test span specified here. In such cases, see Appendix A.3.1 for special considerations and procedures required for testing samples at smaller test spans.

6. Procedures

6.1 Perform the test in the testing atmosphere specified in T 402.

6.2 If the test specimen width is not known to 0.1 mm (0.004 in.) (i.e., if a previously evaluated precision cutter is not used), determine width and parallelism using magnifier and scale. Lack of parallelism is indicated by a difference in width of the two ends of the specimen.

6.3 The testing machine shall be calibrated and adjusted as described in Appendixes A.1 and A.2.

6.4 Set the clamps to an initial test span (distance between line contacts) of 180 ± 5 mm (7.1 ± 0.2 in.). Determine and always reset this distance within ±0.5 mm (0.02 in.) (see Appendix A.1.3).

6.5 Set the controls for rate of separation of the jaws to 25 ± 5 mm/min (1.0 ± 0.2 in./min). In cases where the time required to break a single strip exceeds 30 s, a more rapid rate of jaw separation shall be used, such that the time to break a single strip will be between 15 and 30 s. In such cases, the speed of the instrument must be reported, along with the test data.

NOTE 6: For purposes of determining shipping sack and shipping sack paper TEA compliance with Carrier and Federal requirements, Uniform Freight Classification Rule 40, National Motor Freight Classification, Item 200, UUS 48 and Department of Transportation 178.236, 4.8 in. (122 mm) between the jaws and 1 in. (25 mm) per minute jaw separation should be used.

6.6 Select recorder speed or indicator to give a readability equivalent to 0.05% stretch.

6.7 Select the full scale reading, if possible, so that

breaking force can be read in the upper three-fourths of the scale. Make preliminary trial tests if necessary to determine full scale load.

NOTE 7: If, for any reason, any of the testing conditions specified above (specimen length, rate of jaw separation, sample width, etc.) cannot be followed because of the small sample size or other reason, the method variance *must* be stated in the report.

6.8 Align and clamp the specimen first in one jaw and then, after carefully removing any noticeable slack, in the second jaw. While handling the test specimen, avoid touching the test area between the jaws with the fingers. Use a clamping pressure determined to be satisfactory (Appendix A.1.4), i.e., so that neither slippage nor damage to the specimen occurs.

6.9 Test 10 specimens in each principal direction for each test unit.

6.10 Reject any value in which the test specimen slips in the jaws, breaks within the clamping area, or shows evidence of uneven stretching across its width. Also reject any values for test specimens which break within 5 mm of the clamp area if further inspection indicates the break location is due to improper clamping conditions or misalignment. If more than 20% of the specimens for a given sample are rejected, reject all readings obtained for that sample, inspect the apparatus for conformance with specifications, and take any steps necessary to correct the trouble.

6.11 Read and record the breaking force to 0.5% of full scale and the elongation at break to the equivalent of 0.05% stretch. Record the integrator reading or use the planimeter to determine the area under the load-elongation curve from zero load to the breaking load.

NOTE 8: For the purpose of terminating integration, the specimen will be deemed broken when maximum tensile load has been reached and the tensile load has dropped no more than 0.25% of the full-scale load below the maximum load. This procedure is applicable in the determination of TEA as long as maximum strain occurs at rupture, which is usually the case.

7. Calculations

7.1 For each test unit and in each principal direction, calculate from the recorded values the average breaking force, average elongation at break, and the average integrator or planimeter value as required. Correct the instrumental results, if necessary, according to the correction curve described in the Appendix (A.2.2). Corrections for instrumental deflection need to be applied to both the elongation and energy measurements. Determine the range or standard deviation in each case.

7.2 Divide the average breaking force by the specimen width to obtain the tensile strength. If this has been measured in pounds and inches, convert to kN/m by multiplying by 0.1751. If this has been measured in kg/mm, convert to kN/m by multiplying by 9.807.

NOTE 9: To calculate the breaking length (air dry) in meters use the following formula:

$$BL = 102{,}000\ (T/R) = 3658\ (T'/R')$$

To calculate the tensile index in newton meters per gram use the following formulas:

$$TI = 1000\ (T/R) = 36.87\ (T'/R')$$

where

TI = tensile index, N·m/g
BL = breaking length, m
T = tensile strength, kN/m
T' = tensile strength, lbf/in.
R = grammage (air dry), g/m^2
R' = mass per unit area (air dry), lb/1000 ft^2

7.3 To calculate the percentage stretch, divide the average elongation at break by the test span and multiply by 100.

7.4 Multiply the average integrator or planimeter value by the appropriate factor for the equipment and settings used to obtain the area under the load-elongation curve (Note 6) in energy units, joules (preferred) or inch-pound force. Then calculate the tensile energy absorption, according to one of the following formulas:

$$TEA = 10{,}000\ A/LW \text{ or } 980.7\ A'/LW \text{ or } 175.2\ a/lw$$
$$tea = 12\ a/lw$$

where

TEA = tensile energy absorption, J/m^2
L = initial test span, cm
W = specimen width, cm
A = area under load-elongation curve, J
A' = area under load-elongation curve kgf·cm
tea = tensile energy absorption, ft·lbf/ft^2
a = area under load elongation curve, lbf·in.
l = inital test span, in.
w = specimen width, in.

To convert tensile energy absorption in ft·lbf/ft^2 to J/m^2, multiply by 14.60.

NOTE 10: The "area under the load-elongation curve" is the area between the curve and the elongation axis.

7.5 Determine the corresponding ranges or standard deviations from the ranges or standard deviations of the measured values (7.1).

NOTE 11: Hardware/softwear systems are available that will perform all calculations required in the desired units of measurements.

8. Report

8.1 Report for each test unit and in each direction to three significant figures:

8.1.1 The average tensile strength and the range or standard deviation in kN/m and (if desired) in lbf/in.

8.1.2 The average stretch and the range or standard deviation as a percentage.

8.1.3 The average tensile energy absorption and the range or standard deviation in J/m^2 and (if desired) in $ft{\cdot}lbf/ft^2$.

8.2 Report, in each case, the number of tests rejected and the reasons for rejection.

8.3 Report any deviation in test procedure, as when a short specimen must be used, alternate clamping configurations are used, a wide or narrow strip was tested, or when the rate of jaw separation was varied from 25 ± 5 mm/min (1.0 ± 0.2 in./min) as described in 6.5.

9. Precision

9.1 On the basis of studies (*3*) made in accordance with TAPPI T 1200 "Interlaboratory Evaluation of Test Methods," two test results, each representing an average of 10 determinations, from the same or different samples as noted, are expected to agree within the amounts shown in Table 1.

Table 1. 95% probability limits

	*Tensile strength**, %	*Stretch**, %	*TEA**, %
Repeatability (same sample, operator and apparatus)	5	9	10–16
Comparability (samples markedly different in other properties, but not in designated property, same operator and apparatus)	9	16	15–26
Reproducibility (same sample, different laboratories)	10	25	22–36

*Percentage of the average of the two results.

9.2 In each case, the coefficient of variation of a test result (average of 10 determinations) is expected to be about 0.36 times the value shown in Table 1.

10. Additional information

10.1 Effective date of issue: January 29, 1988.

10.2 This test method may be used in place of the similar method for tensile strength and stretch (T 404) which uses a different type tensile testing machine. These methods are not strictly comparable in that different instrument types are used, but when similar testing conditions are used, they may give similar results. This test method permits three tests (tensile breaking strength, tensile energy absorption, and elongation at break) to be run simultaneously on the same test specimen. This test method also gives more detailed requirements for the apparatus (standardizing on the constant-rate-of-elongation apparatus) and more detailed instructions for the procedure.

10.3 In the modernized metric system, or System International (SI), the units of force and energy are newton (N) and joule (J), respectively. The factors for conversion from the relevant customary units to SI units are as follows:

Force:
1 lbf = 4.448 N
1 kgf = 9.807 N

Energy:
1 N·m = 1.000 J
1 ft·lbf = 1.356 J
1 m·kgf = 9.807 J

Tensile strength:
1 lbf/in. = 0.175 kN/m
1 kgf/15 mm = 0.654 kN/m

Tensile index:
The breaking length in meters is numerically equal to 102 times tensile index in newton meters per gram.

Tensile energy absorption:
1 $ft{\cdot}lbf/ft^2$ = 14.60 J/m^2

10.4 This method was first published in 1964 as a Suggested Method and became an Official Standard in 197[illegible].

10.5 Related methods: ASTM D828 "Tensile Breaking Strength for Paper and Paperboard," American Society for Testing and Materials, Philadelphia, PA; APPITA P 425 "Tensile Strength of Shipping Sack Paper (25.4 mm width)," Technical Association of the Australian and New Zealand Pulp and Paper Industry, Parkville, Australia; BS 4415, British Standards Institution, London, England; CPPA D-34 "Tensile Breaking Strength of Paper and Paperboard," Canadian Pulp and Paper Association, Montreal, Canada; AFNOR QO 3-001, Association Francaise de Normalisation, Paris, France; VXPCI, V12, Zellcheming, Rheinstrasse, Germany; ISO 1924, "Paper and Board, Determination of Tensile Strength," International Organization for Standardization, Geneva, Switzerland; SCAN P 16, "Tensile Strength and Stretch of Paper and Paperboard, Determined with a Pendulum Tester," Scandinavian Pulp, Paper, and Board Testing Committee, Stockholm, Sweden.

Appendix

A.1 *Adjustment and maintenance of testing machine*

A.1.1 Regularly inspect the machine for cleanliness and for faults such as wear, misalignment, loose parts, and damage. Clean the machine and rectify any faults.

A.1.2 Level the machine accurately in its two principal directions. Align the clamping jaws to hold the specimen in the plane of the applied load throughout the test.

A.1.3 Position the jaws so that the test span is as specified (6.4). Verify by measuring effective test span, e.g., by measuring the distance between the centers of the line clamp impressions produced on strips of thin foil.

A.1.4 Determine appropriate clamping pressure so that neither slippage nor specimen damage occurs.

NOTE 12: Papers prepared from the more highly hydrated or beaten stocks, such as tracing paper or glassine, present the most difficult gripping problem. Thus, it is recommended that the clamping pressure be adjusted by making a test with a strong tracing paper. The clamping pressure adjusted to give satisfactory results with this wide variety of papers in the intermediate weight and strength range. The use of excessively high pressure is shown by straightline breaks in, and immediately adjacent to, the clamping zone; whereas the use of too low a pressure shows an abrupt discontinuity in the load-elongation curve, or failure of the specimen beyond the clamped zone, or, following the test, a wider-than-nonnal impression of the clamping line.

A.2 *Calibration of testing machine*

A.2.1 After leveling the machine accurately, calibrate the load measuring mechanism with standard weights by the dead-weight method; i.e., obtain readings at about ten points evenly spaced throughout the scale, by applying known weights with increasing then decreasing increments to the clamp actuating the indicating or recording mechanism. Note the scale readings when the weights and mechanism come gently into the equilibrium position. If readings differ from the corresponding applied loads by more than 0.5%, construct a correction curve.

NOTE 13: This method is only applicable for vertical tensile instruments. For horizontal instruments, follow recommended manufacturer's procedures.

A.2.2 Calibrate the extension measuring mechanism with inside vernier calipers or other appropriate means over the entire load range of interest (*1*). Read the elongation scale at a number of points evenly spaced over the range from about 1 to 20% strain. If readings are in error by more than 0.1% strain, construct a correction curve.

A.3 *Modifications of procedure (and effects thereof)*

A.3.1 *Test specimens*

A.3.1.1 If undersized specimens must be used (e.g., because of size of sample sheets), use 25 mm (preferred) or 15 mm width and lengths long enough to be clamped in jaws either 100 ± 5 mm (4 ± 0.2 in.) or 50 ± 2 mm (2 ± 0.1 in.) apart.

A.3.1.2 The shorter test spans will give higher readings, and it is difficult to measure the elongation accurately [see the Pierce weak-link theory (*4*)]. For papers which have a poor formation, the difference between a test span of 100 mm and the standard span of 180 mm may amount to over 10% in tensile strength and TEA.

NOTE 14: The tensile breaking load, and consequently the breaking strain and TEA, is known to decrease as the test span is increased. The decrease occurs because (1) tensile specimens fail at the weakest part along their length, and (2) as the test length is increased the probability of including a still weaker part also increases.

The effect of test span on breaking load of paper has been found (*1*) to follow the Pierce (*2*) weak-link theory which states that:

$$F_{rL}/F_L = 1\text{-}4.2(1 - r^{-0.2})V/100$$

where:

F_L = breaking load at span L
F_{rL} = breaking load at span rL
V = Coefficient of variation at span L

The table shows the predicted change in tensile breaking load at several test spans and levels of variability, relative to the breaking load at a test span of 200 mm.

Coefficient of variation, %	Predicted change in breaking load, %				
	50 mm span	100 mm span	200 mm span	300 mm span	400 mm span
2	2.7	1.2	—	−0.7	−1.1
4	5.4	2.5	—	−1.3	−2.2
6	8.0	3.7	—	−2.0	−3.3
8	10.7	5.0	—	−2.6	−4.3
10	13.4	6.2	—	−3.3	−5.4

References

1. *Tappi* 47 (1): 47-54 (January 1964).
2. *Journal Textile Inst.* 17: T355-368 (1926).

A.3.1.3 Varying the width of the test specimen between 12 mm and 50 mm does not, in general, make much difference in test results except for unbeaten long-fiber papers, when the difference may be appreciable.

A.3.2.1 *Procedure*

A.3.2.1 At shorter test spans, adjust the rate of jaw separation so that the strain rate matches that achieved with the test span and rate specified in 6.4 and 6.5. This strain rate (rate of jaw separation/test span) is 0.14 ± 0.04 (mm/min / mm). For example, if only one-half (90 mm) of the specified test span were used, the test speed would be set at one-half (12.5 mm/min) of the specified speed.

A.3.2.2 Doubling the test speed (for same length specimen) will increase the apparent tensile strength and may increase TEA for some papers approximately 3%. In other cases stretch will be reduced, thus acting to keep TEA nearly constant.

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1. Van den Akker, J.A., and Hardacker, K.W., "Instrument Studies. LXXXI. The Automatic Recording of the Load Elongation Characteristics of Paper. III. The Table Top Model Instron (Universal Testing Machine)," *Tappi* 41 (8): 224A (1958).
2. Wink, W.A., Hardacker, K. W., and Van Eperen, R.H., "The IPC Line Type Specimen Clamps," *Tappi* 47 (1): 13 (1964).
3. Lashof, T. W., "Precision of Methods for Measuring Tensile Strength, Stretch, and Tensile Energy Absorption of Paper, " *Tappi* 45 (1): 52 (1963).
4. Midgely, E., and Pierce, F. T., *Text. Inst. J.* 17: T355 (1926).

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Technical Divisions Administrator.

H. Bansa und H. H. Hofer

Die Beschreibung der Benutzbarkeitsqualität gealterter Papiere in Bibliotheken und Archiven

Zusammenfassung

Die Beschreibung der Benutzbarkeitsqualität gealterter Papiere in Bibliotheken und Archiven

19 ausgewählte Papiere, teils fabrikneue, großerenteils gebrauchte aus Büchern der Bibliothek, werden subjektiv auf ihre „Benutzbarkeitsqualität" hin untersucht und beurteilt. Sodann wird versucht, diese Benutzbarkeitsqualität meßtechnisch zu beschreiben. Eine der in Frage kommenden Meßmethoden, die Messung der Bruchlast nach einfacher Falzung in einem neu entwickelten Gerät, wird als gut geeignet für die Beschreibung der Benutzbarkeitsqualität gealterter Papiere in Bibliothek und Archiv empfohlen.

Summary

The Description of Usability Characteristics of Aged Papers in Libraries and Archives

19 selected papers, partly new but for the most part used, from books of the library are examined subjectively as to their „usability characteristics". Subsequently it is tried to describe these usability characteristics by measurement. One of the measuring methods in question — that is measurement of tensile strength following single folding in a newly developed device — is recommended for the description of the usability characteristics o aged papers in libraries and archives.

Résumé

La description de la qualité d'aptitude à l'usage de papier vieillis dans les bibliothèques et les archives

On examine et évalue subjectivement 19 papiers choisis, pou une part sortant de l'usine, pour une plus grande part usagé provenant de livres de la bibliothèque, du point de vue de leu „qualité d'aptitude à l'usage". Ensuite on essaie de décrire cett qualité d'aptitude à l'usage en termes de métrologie. L'une de méthodes de mesure entrant en ligne de compte, la mesure de l charge de rupture après pliage simple dans un appareil nouvelle ment mis au point, est recommandée comme bien appropriée à la description de la qualité d'aptitude à l'usage de papiers vieilli dans les bibliothèques et les archives.

Die Papierindustrie und die Papierverarbeitung bezie hungsweise die einschlägige Forschung haben seit Schop per, Herzberg und Brecht eine Fülle von Methoden erar beitet, nach denen die mechanisch-physikalischen Eiger schaften von Papier gemessen und in reproduzierbare Weise mit Zahlen beschrieben werden können. Diese Me thoden erfassen ausnahmslos das hohe Festigkeitsnivea neuer Papiere, die relativ hohen mechanischen Belastur gen ausgesetzt werden, sei es als Verpackung, sei es i einer schnellaufenden Druck- oder Verarbeitungsma schine. Die relativ geringe mechanische Belastung, de ein Papier bei der Benutzung als Datenträger durch Aug und Hand des Menschen unterliegt, läßt sich mit diese Methoden nur unvollkommen erfassen und differenzier beschreiben. Eine von ihnen, die Falzzahl, meist gemes sen mit dem MIT-Tester[1], hat breiten Eingang in die Fo schung zur Papierkonservierung gefunden, ohne Rück sicht auf die Irrelevanz ihrer Aussage für die „Benutz barkeit" von Papier und führte deshalb zu allerlei Miß verständnissen[2]. In der Tat können Papiere mit Falz zahl 0 noch voll benutzbar sein, und hinsichtlich de „Benutzbarkeit" besteht kein Unterschied zwische Falzzahl 50 und 5000. Es wurde deshalb seitens de mehr auf die Praxis der Konservierung und Restaurie

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DESCRIPTION OF USABILITY CHARACTERISTICS OF AGED PAPERS IN LIBRARIES AND ARCHIVES

The paper and paper processing industry and the relevant research have, since Schopper, Herzberg and Brecht, developed a large number of methods by which the mechanical and physical properties of paper can be measured and described with figures in a reproducible manner. These methods without exception detect the high strength level of new paper which is subjected to relatively high mechanical stresses, whether as packing or whether in a high-speed printing or processing machine. The relatively low mechanical stress to which paper is subject at human hands when used as a data carrier, can be detected and described with differentiation only incompletely with these methods. One of them, the folding strength, usually measured with the MIT tester[1], has become widely used in research on paper conservation, without regard to the irrelevance of its information for the "usability" of paper, and has thus led to all kinds of misunderstandings[2]. In actual fact, paper with a folding strength of 0 may still be fully usable, and with respect to "usability" there is no difference between folding strengths of 50 and 5000. It was therefore attempted by the research, which was more oriented towards the practice of conserving and restoring paper in libraries and archives, to find more informative testing methods. The fatigue bending strength[3] and the combination of folding with measurement of breaking load[4,7] were proposed.

In preparation for the work on a community project promoted by the Volkswagenwerk foundation on "The ageing resistance of paper, its principles in natural science and the control of it by restoration and conservation measures," in which the Lower Saxon State Archive in Bückeburg, the Institute for Macromolecular Chemistry of Darmstadt Technical College, the Institute for Book and Manuscript Restoration of the Bavarian State Library in Munich and the Herzog August Library in Wolfenbüttel are participating, it was attempted to put these two methods of measuring and describing

the "usability characteristics" of aged paper in libraries and archives into concrete form on a wider basis.

This wider basis was 19 papers in the most varied states of preservation:

No. 1: brand new nopaset printing paper 60 g/m² from the firm Nordland (Dorpen)

No. 2: brand new printing paper 80 g/m² wood-free from the firm PWA (Redenfelden)

No. 3: brand new newsprint paper 80 g/m² from the firm Haindl (Augsburg)

No. 4: brand new filter paper No. 589² from the firm Schleicher & Schüll (Dassel)

No. 5: lower-grade rag paper: W. Heinsius, Allgemeines Bücher-Lexicon, Leipzig: Brockhaus 1848

No. 6: high-grade historical rag paper: Caesar, De bello Gallico etc. Florence: Ph. Giunta, 1508

No. 7: usable wood paper: Die grosse Politik der europäischen Kabinette 1871-1914, volume 9, Berlin: Deutsche Verlagsanstalt für Politik und Geschichte, 1923

No. 8: wood paper brittle at the fold: Katalog der Bibliothek des ... J.J.J. von Döllinger, Munich: Lindauer, 1893

No. 9: unused, cold-stored copy of the same publication as No. 8

No. 10: coated paper from the 1920's. German-Hungarian publication which cannot be defined in more detail

No. 11: usable wood-containing paper: H. Stegemann, Geschichte des Krieges, volume 2, 111,000-120,000, Stuttgart, Berlin: Deutsche Verlagsanstalt, 1918

No. 12: no longer usable wood-containing paper: Journal des Economistes, Séries IV, volume 26, Paris: Guillaumin, 1884

No. 13: no longer usable rag paper of the 19th century: Séances et travaux de l'Académie des Sciences morales et politiques, compte rendu, vol. 55, Paris: A. Durand, 1861

No. 14: no longer usable paper: Annual directory of papers published at German universities, I, Berlin: Asher 1887

No. 15: endangered wood-containing paper: Ergebnisse der Vitamin- und Hormonforschung, I, Berlin: Akad. Verlagsges. 1938

No. 16: paper which can be used normally: Biologisches Centralblatt 26, Erlangen: Besold 1906

No. 17: historical rag paper which can be used normally: J.B. Haydt, Kurtzer Begriff ... des Heiligen Nicolai von Tolentin, Ingolstadt: Th. Grass 1694

No. 18: well preserved rag paper of the 19th century: Blackwood's Edinburgh Magazine, vol. 69, no. 424, London, Edinburgh: Blackwood 1854

No. 19: strong paper: R. Amundsen, Die Eroberung des Südpols, 1, Munich: Lehmann 1912.

In order to give a more detailed idea of the quality of these papers, some measurement and analysis values are given in Table 1.

The 19 papers were first assessed subjectively for their quality by three persons - restoration experts or librarians whose professional task it is to monitor the "usability" of paper in books and restore it if it is lost. So-called "pair comparison" was used for this. Here, any two samples are compared with each other and graded one against the other as "better," "same" or "worse." When carried out systematically, for each sample a double assessment is obtained, correct averaging of which allows grading. The assessment of the 19 papers resulting from assessment by three restoration experts or librarians is compiled in Table 2.

Subjective assessment leads to differences in grading in case of all three testers. In case of samples which are hardly usable any more (grade number = 16 to 19), on the other hand, considerable agreement is observed. To check whether these gradings made by several observers can also be regarded as definite, viewed statistically, Kendall's agreement factor W[5,6] is suitable, to calculate which the formulae given in Appendix 1 must be used. Testing the gradings given in Table 2, lines 1-3, yields $W=0.9297$. Thus there is agreement between the assessments by the three testers with a statistical certainty of more than 99.9%. The grading given in Table 2, line 4 as the mean value of the three assessments can thus be used as standard classification for further discussion.

It was now a question of obtaining this standard classification by measurement techniques. For the sake of completeness, at first

we did not confine ourselves to the two methods mentioned at the beginning, which seem suitable for this (fatigue bending strength and breaking load after folding), but included the Schopper double fold number and compressive folding according to Brecht-Wesp[7].

From Table 3, line 1, can be seen the well-known fact that the Schopper double fold number is not suitable for describing the usability characteristics of paper in books. Lines 3 and 5 show that for pre-folding followed by measurement of breaking load, the compressive folder according to Brecht-Wesp is perfectly suitable. But according to information from the firm Frank (Weinheim), the apparatus is no longer built. Also it requires larger samples (strip length at least 16 cm), the provision of which may mean a problem in case of old paper from used (cut) books. Thirdly, in the lower range the method always differentiates less well than measurement of breaking load after single folding, which is described below. We therefore dispensed with pursuing it further.

With the apparatus for measuring fatigue bending strength, the load can be varied, and also the angle of bending can be selected differently. It is only with difficulty that the angle of bending can be adjusted reproducibly; it must therefore be fixed and stay the same for the whole measurement series. On the basis of preliminary tests it was fixed at 30°. The load was adapted to the condition of the material in stages to speed up measurement at high strength, and to obtain more informative, not too low figures at low strength. This is simple and reproducible. With a bending angle of 30°, the following graduation proved to be significant (see also Figs. 1 and 2):

0.490 N $\hat{=}$ 50 g
2.943 N $\hat{=}$ 300 g
7.848 N $\hat{=}$ 800 g
14.715 N $\hat{=}$ 1,500 g

Table 4 contains the fatigue bending strengths of paper strips 15 mm wide of the 19 samples under the different loads, this being in case of the higher one only if at the lower one it was more than 1,000 three times consecutively.

The grade numbers which result from measurement of the fatigue

bending strength as described are not the same for longitudinal and transverse directions of the same paper. To produce comparability with the standard classification, which makes no difference between the directions, the mean value was calculated after longitudinal and transverse directions yielded identical grades with statistical certainty. Table 4, line 11 compares this mean value with the standard classification (line 12). These grades tally with a statistical certainty of more than 99.9%. Thus it is established that by determining the fatigue bending strength, a significant assessment of "usability" of paper is possible.

To measure the breaking load after folding, first it was a question of defining this fold reproducibly. After preliminary tests it was decided to design and build an oblique plane which forms an angle of 20° with the horizontal. The folding roller with a weight of 500 g rolls over it and after the designated rolling distance of 30 cm folds the paper by rolling over it (see Figs. 3 and 4). The paper is mounted in such a way that there is no prior creasing of the test strip. It is adjustable in angle of inclination to allow it to lie satisfactorily in the roller path. The load during folding is 4.25 N, which corresponds to a linear pressure of 283.19 N/m for a test strip width of 15 mm. The test results for breaking load are compiled in Table 5, and those for breaking load after folding are compiled in Table 6.

The breaking load without folding already shows a correlation with the standard classification (Table 5, line 9; ρ=0.7952). The correlation becomes considerably better by folding under the conditions described here, followed by measurement of breaking load. This yields a Spearman coefficient of grade correlation[5] (see Appendix 2) of ρ=0.9132 (Table 6, line 9).

Thus the correlation with breaking load values after folding is even better than with determination of fatigue bending strengths (ρ=0.8807), the two coefficients of grade correlation displaying agreement with the standard classification of more than 99.9% statistical certainty. This means that both fatigue bending strength and breaking load after folding can be used according to the method described here to assess usability of paper in archives and librar-

ies. Determination of fatigue bending strength clearly requires much more effort than determination of breaking load after folding.

Both methods gave relatively large spreads of measured values for the individual papers; the standard deviations from 10 measurements may be 50% of the measured values or more. Nevertheless, allowing for the standard deviation (lines 3/4 and 7/8 in Tables 5 and 6) did not produce any improved correlation with the standard classification, so that it is proposed to dispense with taking the standard deviation into consideration when assessing the usability of aged paper by measurement. It was also checked whether taking the breaking load before folding into consideration, perhaps by calculating the decrease in breaking load by folding, produces an improvement in the correlation with the standard classification of the papers. This was not the case. The average breaking load after folding out of a statistically large enough number of test strips 15 x 100 mm thus proved to be the best basis for assessing "usability characteristics" of aged paper in archives and libraries.

The correlation between subjective quality assessment on the one hand and fatigue bending strength or breaking load after folding on the other seems, as stated, definite. To produce for the restoration expert and librarian a correlation between the test results which are abstract figures, and verbal descriptions of condition full of specific images, it was attempted to sort the measured values or grading in the standard classification into "usability classes" which seem meaningful. The result is recorded in Table 7. This shows very clearly the above-mentioned particularly good agreement between breaking load values after folding and the standard classification. The huge deviations can be explained plainly:

1. Papers Nos. 6 and 17 are old, hand-made rag papers, recognisable as such at first glance by the feel, sound and text which they bear, by contrast with the rag papers of the 19th century, Nos. 5 and 18. When assessed by persons who deal mainly with old paper and for whom the expression "hand-made rag paper" presents a positive concept from the start, obviously they were given a "plus

for rags" which constitutes a class compared with the objective quality assessment by measuring breaking load after folding.

2. Paper No. 10, a coated paper, by negative analogy with the rag papers, ought to have been given a "minus for modernisation."

3. Papers Nos. 3, 7, 8, 9, 11 and 15 are wood papers, No. 3 is new, Nos. 7, 8, 9, 11 and 15 are several decades old and yellowed. Only its new condition and lack of yellowing obviously gave No.3 a better subjective assessment than the measured values justify. With the other papers, it seems the yellowed condition affected the subjective assessment. This is most striking with No. 8. Here the decay is fairly well advanced; the paper is brittle and requires restoration - but only at the edge. For this edge, the subjective classification "still usable with care" may be true; for the middle of the sheet, from which the strips for tests were taken, it is not true. It is noteworthy that the difference in quality resulting from different types of storage of the same paper (Nos. 8 and 9), is still detected with measurement of breaking load after folding, just as in the subjective assessment, although on another level.

The latter leads us to hope that measurement of breaking load after folding and sorting the results into usability grades is a fine enough method of describing the condition of library stocks, detecting differences in quality due to storage, describing the success of restoration measures, etc. In addition to the very good correlation with subjective quality assessment it offers the advantage that its values are available quickly and without great cost. A statistically large enough number (10 in each of the two directions, longitudinal and transverse) of test strips 15 mm wide and 100 mm long are pre-folded. Then the breaking load is measured. When assessing "usability characteristics," grading is as follows:

grade I very strong, durable	F>36 N in one or both directions
grade II strong	36 N > F > 12 N in both directions
grade III fully usable	36 N > F > 12 N in one of the two directions
grade IV	12 N > F > 4 N in both directions

usable	
grade V	12 N > F > 4 N in one of the two
still usable (with care)	directions
grade VI	breaking load after folding still
endangered	measurable in both directions
grade VII	breaking load after folding no
no longer usable	longer measurable.

It would be within the analogy of the classification proposed here to extend the scale at the top and bottom by one grade each:

grade 0	F > 36 N in both directions
grade I	F > 36 N in one of the two directions
grade VII	breaking load after folding still measurable in one of the two directions
grade VIII	breaking load after folding no longer measurable in any direction

There is no need for grade 0 in the field of libraries and archives; grade VIII (or grade VII if grade VIII is to be used) is not represented among the 19 samples which form the basis of this work.

It remains to be seen whether research on the art of restoration accepts the measurement and assessment proposed here and whether it proves itself in future.

Appendix 1:

Calculation of the Kendall agreement factor W (5,6)

for N>7 the test variable P is calculated as:

$$P = K (N - 1) W$$

ξ_j = sum of the grade numbers allotted to a sample by the different observers

K = number of observers

N = number of samples

W is close to a value of 1,000 for full agreement.

To indicate the statistical certainty, P must be compared with

the values of χ^2 for n=N-1.

The values of χ^2 are, for N=19 (n=18) with the statistical certainties S indicated:

S = 95 % → χ^2 = 28,869
S = 99 % → χ^2 = 34,805
S = 99.9% → χ^2 = 42,312

Appendix 2:

Calculation of the coefficient of grade correlation according to Spearman (5)

u_j, v_j: grade numbers of product assessment
u - by the first observer
v - by the second observer
N: number of samples

ρ is close to a value of + 1.00 for full agreement of the two observers' assessments.

For N=19 (our example), the test variable P is calculated as:

To indicate the statistical certainty, P must be compared with the integral boundaries of t-distribution for the degree of freedom n=N-2. The integral boundaries have the following values at the statistical certainties S in our example:

S = 95 % → t = 2.11
S = 99 % → t = 2.90
S = 99.9% → t = 3.96.

errichteten Anlagen bzw. ihre Geräte. Insgesamt waren acht finnische Hersteller vertreten. Für die Planung und Gestaltung des Gemeinschaftsstandes waren neben den teilnehmenden Firmen der Außenhandelsverband und das Außenhandelsbüro des Finnischen Generalkonsulats in Frankfurt/Main verantwortlich.

Die Aussteller und ihre Erzeugnisse in Baden-Baden: **Enso-Gutzeit Oy (Savonlinna)**: Twincleaner-Wirbelreiniger zur Stoffreinigung; Ensovac-Systeme zur Entlüftung und Reinigung des Papierstoffes sowie Refiner zur Aufbereitung und Herstellung des Stoffes.

Kajaani GmbH (Starnberg): Cormec In-Line Weißgradmeßgerät; Coram On-Line Weißgradmeßgerät; Polarox Chemikalien-Analysator (z. B. Cl_2, ClO_2, SO_2); Samplex Probenentnahmesystem für Zellstoff (Konzentrationsbereich von 0—16 Prozent).

Kone Oy (Hyvinkää): Holzbehandlungsanlagen, Hebe- und Förderanlagen; Entrindungsanlagen; Automatische Behandlungssysteme für Papierrollen.

Neles (Helsinki): Kugel-Stellventile (Stem Ball) und Stellklapper (Nel-Disc) für Regelung und Absperrbetrieb; Pneumatische Stellantriebe, Stellungsregler, Endlagen-Schalter und Handantriebe.

Nokia GmbH (Helsinki): Automatisierungssysteme für Zellstoffindustrie.

Oy Strömberg AB (Vaasa): Ulma Fehleranalysator für laufende Papierbahnen.

Oy Tampella AB (Tampere): Zellstoff- und Papierindustrie, Energieerzeugung; Verfahrenstechnik.

TVW Papiermaschinen GmbH (Helsinki): 1) Tampella: Kartonmaschinen; Holzschleifereien, Stoffaufbereitungsmaschinen. 2) Valmet: Papiermaschinen; Zellstoffwäscher; Zellstoffmaschinen, Ventilations- und Wärmerückgewinnungseinrichtungen. 3) Wärtsilä: Rollenschneidmaschinen; Streichmaschinen, Rollenpackanlagen, Zellstoffabrikeinrichtungen.

H. Bansa und H. H. Hofer

Die Beschreibung der Benutzbarkeitsqualität gealterter Papiere in Bibliotheken und Archiven

Zusammenfassung

Die Beschreibung der Benutzbarkeitsqualität gealterter Papiere in Bibliotheken und Archiven

19 ausgewählte Papiere, teils fabrikneue, größerenteils gebrauchte aus Büchern der Bibliothek, werden subjektiv auf ihre „Benutzbarkeitsqualität" hin untersucht und beurteilt. Sodann wird versucht, diese Benutzbarkeitsqualität meßtechnisch zu beschreiben. Eine der in Frage kommenden Meßmethoden, die Messung der Bruchlast nach einfacher Falzung in einem neu entwickelten Gerät, wird als gut geeignet für die Beschreibung der Benutzbarkeitsqualität gealterter Papiere in Bibliothek und Archiv empfohlen.

Summary

The Description of Usability Characteristics of Aged Papers in Libraries and Archives

19 selected papers, partly new but for the most part used, from books of the library are examined subjectively as to their „usability characteristics". Subsequently it is tried to describe these usability characteristics by measurement. One of the measuring methods in question — that is measurement of tensile strength following single folding in a newly developed device — is recommended for the description of the usability characteristics of aged papers in libraries and archives.

Résumé

La description de la qualité d'aptitude à l'usage de papiers vieillis dans les bibliothèques et les archives

On examine et évalue subjectivement 19 papiers choisis, pour une part sortant de l'usine, pour une plus grande part usagés provenant de livres de la bibliothèque, du point de vue de leur „qualité d'aptitude à l'usage". Ensuite on essaie de décrire cette qualité d'aptitude à l'usage en termes de métrologie. L'une des méthodes de mesure entrant en ligne de compte, la mesure de la charge de rupture après pliage simple dans un appareil nouvellement mis au point, est recommandée comme bien appropriée à la description de la qualité d'aptitude à l'usage de papiers vieillis dans les bibliothèques et les archives.

Die Papierindustrie und die Papierverarbeitung beziehungsweise die einschlägige Forschung haben seit Schopper, Herzberg und Brecht eine Fülle von Methoden erarbeitet, nach denen die mechanisch-physikalischen Eigenschaften von Papier gemessen und in reproduzierbarer Weise mit Zahlen beschrieben werden können. Diese Methoden erfassen ausnahmslos das hohe Festigkeitsniveau neuer Papiere, die relativ hohen mechanischen Belastungen ausgesetzt werden, sei es als Verpackung, sei es in einer schnellaufenden Druck- oder Verarbeitungsmaschine. Die relativ geringe mechanische Belastung, der ein Papier bei der Benutzung als Datenträger durch Auge und Hand des Menschen unterliegt, läßt sich mit diesen Methoden nur unvollkommen erfassen und differenziert beschreiben. Eine von ihnen, die Falzzahl, meist gemessen mit dem MIT-Tester[1], hat breiten Eingang in die Forschung zur Papierkonservierung gefunden, ohne Rücksicht auf die Irrelevanz ihrer Aussage für die „Benutzbarkeit" von Papier und führte deshalb zu allerlei Mißverständnissen[2]. In der Tat können Papiere mit Falzzahl 0 noch voll benutzbar sein, und hinsichtlich der „Benutzbarkeit" besteht kein Unterschied zwischen Falzzahl 50 und 5000. Es wurde deshalb seitens der mehr auf die Praxis der Konservierung und Restaurie-

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rung von Papier in Bibliotheken und Archiven orientierten Forschung versucht, aussagekräftigere Prüfmethoden zu finden. Vorgeschlagen wurden die Dauerbiegezahl[3] und die Kombination einer Falzung mit der Messung der Bruchlast[4,7].

Als Vorbereitung für die Arbeit an einem von der Stiftung Volkswagenwerk geförderten Gemeinschaftsprojekt über „Die Alterungsbeständigkeit von Papier, ihre naturwissenschaftlichen Grundlagen und ihre Beeinflussung durch restauratorische und konservatorische Maßnahmen", an denen sich das Niedersächsische Staatsarchiv in Bückeburg, das Institut für Makromolekulare Chemie der Technischen Hochschule Darmstadt, das Institut für Buch- und Handschriftenrestaurierung der Bayerischen Staatsbibliothek in München und die Herzog-August-Bibliothek in Wolfenbüttel beteiligen, wurde versucht, diese beiden Methoden der Messung und Beschreibung der „Benutzbarkeitsqualität" gealterter Papiere in Bibliothek und Archiv auf breiterer Grundlage zu konkretisieren.

Diese breitere Grundlage waren 19 Papiere im unterschiedlichsten Erhaltungszustand:

Nr. 1: fabrikneues Druckpapier nopaset 60 g/m² der Firma Nordland (Dörpen)

Nr. 2: fabrikneues Druckpapier 80 g/m² holzfrei der Firma PWA (Redenfelden)

Nr. 3: fabrikneues Zeitungsdruckpapier 80 g/m² der Firma Haindl (Augsburg)

Nr. 4: fabrikneues Filtrierpapier Nr. 589² der Firma Schleicher & Schüll (Dassel)

Nr. 5: minderwertiges Hadernpapier: W. Heinsius, Allgemeines Bücher-Lexicon. Leipzig: Brockhaus 1848

Nr. 6: hochwertiges historisches Hadernpapier: Caesar, De bello Gallico etc. Florenz: Ph. Giunta 1508

Nr. 7: benutzbares Holzschliffpapier: Die große Politik der europäischen Kabinette 1871–1914. Band 9. Berlin: Dt. Verlagsanstalt f. Politik u. Geschichte 1923

Nr. 8: im Falz brüchiges Holzschliffpapier: Katalog der Bibliothek des ... J. J. J. von Döllinger. München: Lindauer 1893

Nr. 9: unbenutztes, kühl gelagertes Exemplar der gleichen Publikation wie Nr. 8

Nr. 10: gestrichenes Papier aus den 20er Jahren des 20. Jh. Nicht näher bestimmbare deutsch-ungarische Publikation

Nr. 11: benutzbares holzhaltiges Papier: H. Stegemann, Geschichte des Krieges Band 2. 111.–120. Tsd. Stuttgart, Berlin: Dt. Verlagsanstalt 1918

Nr. 12: nicht mehr benutzbares holzhaltiges Papier: Journal des Economistes Série IV tom. 26. Paris: Guillaumin 1884

Nr. 13: nicht mehr benutzbares Hadernpapier des 19. Jahrhunderts: Séances et traveaux de l'Académie des Sciences morales et politiques, compte rendu tom. 55. Paris: A. Durand 1861

Nr. 14: nicht mehr benutzbares Papier: Jahres-Verzeichnis der an den deutschen Universitäten erschienenen Schriften I. Berlin: Asher 1887

Nr. 15: gefährdetes holzhaltiges Papier: Ergebnisse der Vitamin- und Hormonforschung I. Berlin: Akad. Verlagsges. 1938

Nr. 16: normal benutzbares Papier: Biologisches Centralblatt 26. Erlangen: Besold 1906

Nr. 17: normal benutzbares historisches Hadernpapier: J. B. Haydt, Kurtzer Begriff ... deß Heiligen Nicolai von Tolentin. Ingolstadt: Th. Graß 1694

Nr. 18: gut erhaltenes Hadernpapier des 19. Jahrhunderts: Blackwood's Edinburgh Magazine vol. 69 No. 424. London, Edinburgh: Blackwood 1854

Nr. 19: festes Papier: R. Amundsen, Die Eroberung des Südpols 1. München: Lehmann 1912

Um eine nähere Vorstellung von der Beschaffenheit dieser Papiere zu vermitteln, werden in Tab. 1 einige Meß- und Analysenwerte mitgeteilt.

Die 19 Papiere wurden zunächst von drei Personen – Restauratoren beziehungsweise Bibliothekaren, deren berufliche Aufgabe es ist, die „Benutzbarkeit" von Papier in Büchern zu überwachen und wiederherzustellen, soweit sie verlorengegangen ist – subjektiv nach ihrer Qualität beurteilt. Dafür wurde der sogenannte „paarweise Vergleich" herangezogen. Dabei werden jeweils zwei Muster miteinander verglichen und eines gegen das andere mit „besser", „gleich" oder „schlechter" eingestuft. Bei systematischer Durchführung erhält man für jedes Muster eine doppelte Beurteilung, deren sinngerechte Mittelung eine Rangeinstufung gestattet. Die aus der Beurteilung durch drei Restauratoren bez. Bibliothekare sich ergebende Beurteilung der 19 Papiere ist in Tab. 2 zusammengefaßt.

Die subjektive Beurteilung führt bei allen drei Prüfern zu Abweichungen in der Einstufung. Bei den kaum mehr brauchbaren Mustern (Rangziffer RZ = 16 bis 19) dagegen beobachtet man weitgehende Übereinstimmung. Zur Überprüfung, ob diese von mehreren Beobachtern erstellten Rangeinstufungen auch statistisch gesehen als gesichert anzusehen sind, eignet sich der Kendall'sche Übereinstimmungskoeffizient W[5,6], zu dessen Berechnung die in Anhang 1 angegebenen Formeln zu verwenden sind. Die Prüfung der in Tab. 2 Zeile 1–3 gegebenen Rangeinstufungen ergibt $W = 0{,}9297$. Damit ist mit einer statistischen Sicherheit von mehr als 99,9 % Übereinstimmung zwischen den Beurteilungen durch die drei Testpersonen gegeben. Die in Tab. 2 Zeile 4 als Mittelwert der drei Beurteilungen gegebene Rangeinstufung kann also für die weitere Diskussion als Standardklassifizierung dienen.

Es galt nun, diese Standardklassifizierung meßtechnisch zu erfassen. Um der Vollständigkeit willen beschränkte man sich zunächst nicht auf die beiden eingangs genannten hierfür geeignet erscheinenden Methoden (Dauerbiegezahl und Bruchlast nach Falzung), sondern bezog auch die Schopper'sche Doppelfalzzahl und die Druckfalzung nach Brecht-Wesp[7] ein.

Aus Tab. 3 Zeile 1 ist die bekannte Tatsache zu ersehen, daß sich die Schopper'sche Doppelfalzzahl zur Beschreibung der Benutzbarkeitsqualität von Papier in Büchern nicht eignet. Zeile 3 und 5 zeigen, daß für eine Vorfalzung mit nachfolgender Messung der Bruchlast der Druckfalzer nach Brecht-Wesp durchaus in Frage käme. Das Gerät wird aber laut Auskunft der Firma Frank (Weinheim) nicht mehr gebaut. Außerdem benötigt es größere Proben (Streifenlänge mindestens 16 cm), deren Bereitstellung bei alten Papieren aus gebrauchten (beschnittenen) Büchern ein Problem bedeuten kann. Zum dritten differenziert die Methode im unteren Bereich in jedem Falle weniger gut als die im Folgenden zu beschreibende Messung der Bruchlast nach einfacher Falzung. Es wurde deshalb darauf verzichtet, sie weiter zu verfolgen.

Tab. 1 Kennzahlen der für den Vergleich herangezogenen Papiere

	Einheiten	Papiernummern 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
1 Flächenbezogene Masse m_A	g/m²	60	80	80	80	60	60	100	70	75	100	85	70	65	80	55	85	70	60	150
2 Faserzusammensetzung (geschätzt)																				
3 Kiefernsulfatz. gebl.	%	40	30												50					
4 Fichtensulfatz. gebl.	%	20	50	20	50															80
5 Fichtensulfitz. gebl.	%							40	20	20	50	30	10			40	40			
6 Birkensulfatz. gebl.	%	40			20															
7 Buchensulfatz. gebl.	%		20								40									
8 Fichtenholzschliff	%			80				60	30	80		60	50			60				
9 Hanf / Flachs	%					100	100				10	10	10	100			20	100	100	20
10 Baumwolle	%				20										10					
11 Strohzellstoff	%												30		40		40			
12 Chemische Analyse																				
13 pH-Wert Oberfläche	pH	7.4	5.5	5.7	4.7	4.7	8.1	4.3	4.4	5.0	7.5	4.3	3.5	3.8	4.2	3.5	3.5	7.0	7.2	4.5
14 pH-Wert Kaltextrakt	pH	7.8	5.1	5.7	5.7	4.8	8.0	4.4	4.5	4.8	7.1	5.8	3.6	4.8	5.1	5.0	4.6	8.0	8.2	5.3
15 pH-Wert Heißextrakt	pH	8.4	5.3	5.2	5.7	4.8	8.7	4.5	4.5	4.7	7.8	5.3	3.7	4.3	5.1	4.5	5.0	8.7	8.7	5.1
16 Pufferkapazität (*)	ml 0,1-n Sr oder A	35.8 Sr	0.5 A	0.25 A	0.65 A	1.2 A	10.45 Sr	1.6 A	1.6 A	1.7 A	1.6 Sr	0.9 A	2.6 A	1.7 A	2.3 A	2.1 A	1.3 A	0.9 Sr	0.4 A	1.6 A
17 Karboxylgruppen	%	0.35	0.27	0.33	0.18	0.42	0.5	0.4	0.52	0.47	0.42	0.32	0.43	0.23	0.25	0.47	0.57	0.36	0.3	0.24
18 Asche	%	16.1	15.8	30.9	0	0.9	5.7	31.2	11.9	12.0	26.5	30.4	20.1	20.0	10.9	9.6	23.8	2.0	0.8	27.5
19 Mg	%	0.2	0.1	0.3	0	0	0	0.2	0.1	0	0	0	0	0	0	0	0	0	0	0
20 Ca	%	10.3	0.3	0.2	0	0.4	3.3	4.2	0.4	0.4	2.7	0.2	0.3	0.3	0.6	0.4	0.3	0.8	0.5	0.4
21 Ba	%	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
22 Al	%	0	3.3	6.5	0	0	0	2.7	2.0	2.7	3.4	6.2	4.0	4.9	2.2	2.2	4.5	0	0	5.4
23 Fe	%	0.04	0.05	0.15	0	0	0.06	0	0.06	0.1	0.1	0	0.13	0.12	0.06	0.1	0.12	0.05	0	0.13
24 Cu	%	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
25 SO_4^{2-}	%	0	0.3	0	0	0.1	0.4	9.7	0	0	4.3	0	0.4	0.25	0	0.3	0	0	0	0
26 SiO_2	%	1.0	7.5	14.0	0	0.1	0.7	6.5	6.6	6.5	6.0	18.0	10.0	15.0	5.5	5.5	14.5	0.5	0.06	16.0

(*) Kaltextrakt aus 1 g Papier mit 50 ml 0,1-n HCl

Angegeben werden die vom Papier verbrauchten ml 0,1-n HCl (Sr) bzw. 0,1-n NaOH (A) in Analogie zu Säurezahl oder Alkalizahl

Tab. 2 Beurteilung der Benutzbarkeit der 19 untersuchten Papierqualitäten durch Bibliothekare und Restauratoren der Bayerischen Staatsbibliothek mit Hilfe des „paarweisen Vergleichs" – Angabe der Qualität in Rangstufen (Rangstufe 1 = bestes Muster, Rangstufe 19 = schlechtestes Muster, gleiche Rangstufen bedeuten gleiche Beurteilung)

	Papier Nr.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
1	Bibliothekar	4	4	8.5	2	14	1	11	13	12	10	8.5	19	18	17	16	15	7	4	6
2	Restaurator 1	2	1	8	4.5	16	3	9.5	13	9.5	6.5	11	18	19	17	14	12	15	6.5	4.5
3	Restaurator 2	3.5	3.5	6	1	14	2	12.5	15.5	11	10	7	18.5	18.5	15.5	17	12.5	8	9	5
4	Mittelwert	4	3	7	2	15	1	12	14	11	8.5	8.5	18.5	18.5	17	16	13	10	6	5

Tab. 3 Doppelfalzung nach Schopper und Druckfalzung nach Brecht-Wesp (25 Falzungen) der untersuchten Papierproben

Z.	Papiernummern		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
1	Doppelfalzung (n) (Schopper)	MD	70	135	7	15	0.3	n.m.	1	1	3	n.m.	2	0	0	0	0	1	0	5	2
		CD	78	19	2	7	0	n.m.	1	1	2	n.m.	2	0	0	0	0	1	0	5	2
2	Bruchlast (N)	MD	74.16	73.3	39.82	37.74	10.73	32.23	30.94	18.48	23.49	49.94	40.35	10.33	8.9	24.46	26.74	35.16	7.36	41.74	53.46
3	Bruchlast n. Druckfalzung (N) (Brecht-Wesp)	MD	47.82	53.85	23.51	24.46	15.7	n.m.	13.77	n.m.	n.m.	n.m.	19.55	0	0	0	n.m.	0	5.13	n.m.	22.35
4	Bruchlast (N)	CD	45.4	31.35	13.01	28.61	2.8	23.60	19.25	12.73	15.57	21.39	17.04	7.52	5.23	17.6	13.22	17.48	5.78	17.99	44.59
5	Bruchlast n. Druckfalzung (N) (Brecht-Wesp)	CD	34.25	25.55	0	19.76	9.86	14.56	7.54	9.08	9.78	n.m.	10.56	0	0	0	0	n.m.	0	12.02	18.41

n.m. = vorliegende Papierproben waren für die Prüfung zu kurz

Bei dem Gerät zur Messung der Dauerbiegezahl kann man die Belastung variieren, und auch der Biegewinkel kann verschieden gewählt werden. Der Biegewinkel ist nur mit Aufwand reproduzierbar verschieden einzustellen; er muß deshalb für die ganze Meßreihe feststehen und gleichbleiben. Basierend auf Vorversuchen wurde er auf 30° festgelegt. Die Belastung wurde zur Beschleunigung der Messung bei hoher und zum Erreichen aussagekräftiger, nicht zu kleiner Zahlen bei niedriger Festigkeit stufenweise dem Materialzustand angepaßt. Dies ist einfach und reproduzierbar möglich. Bei einem Biegewinkel von 30° erwies sich folgende Stufung als sinnvoll (siehe auch Abb. 1 und 2)

0,490 N ≙ 50 g
2,943 N ≙ 300 g
7,848 N ≙ 800 g
14,7150 N ≙ 1 500 g

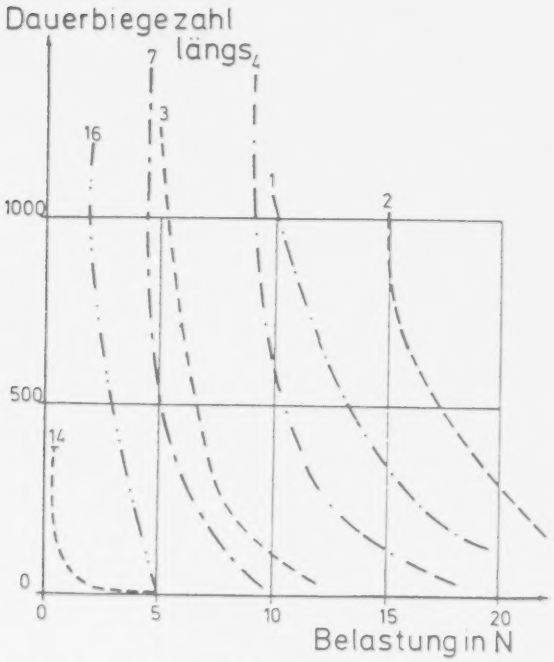

Abb. 1 Abhängigkeit der Dauerbiegezahlen ausgewählter Muster von der Belastung. Dauerbiegezahl längs

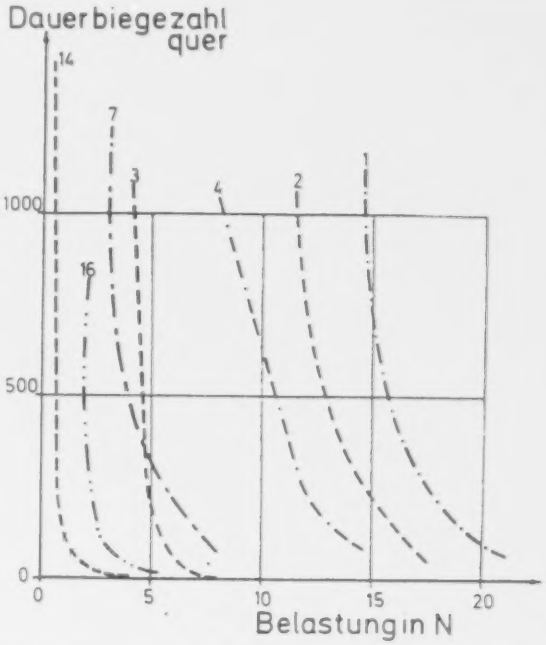

Abb. 2 Abhängigkeit der Dauerbiegezahlen ausgewählter Muster von der Belastung. Dauerbiegezahl quer

Tab. 4 enthält die Dauerbiegezahlen von Papierstreifen mit 15 mm Breite der 19 Muster bei den verschiedenen Belastungen, und zwar bei der jeweils höheren nur, wenn sie bei der niederen dreimal hintereinander größer war als 1 000.

Die Rangziffern, die sich aus der geschilderten Messung der Dauerbiegezahl ergeben, sind für Lauf- und Querrichtung des gleichen Papiers nicht gleich. Zum Herstellen der Vergleichbarkeit mit der Standardklassifizierung, die keinen Unterschied zwischen den Richtungen macht, wurde der Mittelwert errechnet, nachdem Lauf- und Querrichtung statistisch gesichert übereinstimmende Einstufung ergaben. Tab. 4 Zeile 11 stellt diesen Mittelwert der Standardklassifizierung (Z. 12) gegenüber. Diese Einstufungen stimmen mit einer statistischen Sicherheit von mehr als 99,9 % überein. Damit ist festgestellt, daß durch die Bestimmung der Dauerbiegezahl eine sinnvolle Beurteilung der „Benutzbarkeit" eines Papiers möglich ist.

Tab. 4 Messung der Dauerbiegezahlen der 19 Papiersorten bei einem Biegewinkel von ± 30° und stufenweiser Belastung mit F = 14,715 N; 7,848 N; 2,943 N; 0,490 N

Zeile	Papier Nr.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
	Laufrichtung																			
1	F_4 = 14,715 N	470	1029	–	217	–	216	–			–	–								
2	F_3 = 7,848 N	>1000	>1000	221	>1000	517	>1000	92	79	75	526	242	1	1		78	1	5	542	289
3	F_2 = 2,943 N	–		>1000		>1000	–	>1000	>1000	>1000	>1000	>1000	1	1	5	504	3(x)	15	>1000	>1000
4	F_1 = 0,490 N	–	–	–	–	–	–	–	–	–	–	–	1	5	>1	>1000	>1000	>1000		
5	Rangziffer	2	1	10	3	8	2	11	11	12	7	5,5	19	18	11	14	15	16	13	9
	Querrichtung																			
6	F_4 = 14,715 N	813	230	–	–	–	–	–			–	–								
7	F_3 = 7,848 N	>1000	>1000	15	>1000	1342	629	75	55	22	64	91	1	2	1	2	8	1	56	33
8	F_2 = 2,943 N			>1000	–	573	>1000	>1000	>1000	>1000	>1000	>1000	1	1	5	147	111	172	>1000	1
9	F_1 = 0,490 N	–	–	–	–	>1000	–	–	–	–	–	–	1	5	>1000	>1000	>1000	>1000		
10	Rangziffer	1	2	12	3	12	4	8	9,5	11	7	6	19	18	11	15	16	14	9,5	9
11	Rangziffer (Mittelwert)	1,5	1,5	11	3,5	10	3,5	9	12	13	6,5	5	19	18	11	15	16	14	9,5	9
12	Benutzbarkeit (Tab. 1 Z 4)	4	3	7	2	15	1	12	14	11	6,5	6,5	18,5	18,5	10	16	17	8	3	3

Spearman'scher Rangkorrelationskoeffizient Zeile 5–10 $\rho = 0{,}9180$
11–12 $\rho = 0{,}8807$

Zur Messung der Bruchlast nach Falzung galt es zunächst, diese Falzung reproduzierbar zu definieren. Nach Vorversuchen entschied man sich zu Konstruktion und Bau einer schiefen Ebene, die mit der Horizontalen einen Winkel von 20° bildet. Über sie rollt die Falzwalze mit einer Masse von 500 g ab und falzt nach der definierten Rollstrecke von 30 cm das Papier durch Überrollen (s. Abb. 3 und 4). Die Papiereinspannung ist dabei so ausgebildet, daß keinerlei Vorknicken der Probestreifen erfolgt. In der Neigung ist sie justierbar, um ein einwandfreies Aufliegen in der Rollbahn zu ermöglichen. Die Belastung beim Falzen beträgt 4,25 N, das entspricht einem Liniendruck von 283,19 N/m bei einer Prüfstreifenbreite von 15 mm. Die Meßergebnisse für die Bruchlast sind in Tab. 5, die für die Bruchlast nach Falzung sind in Tab. 6 zusammengefaßt.

Bereits die Bruchlast ohne Falzung zeigt eine Korrelation zur Standardklassifizierung (Tab. 5 Zeile 9, $\rho = 0{,}7952$). Die Korrelation wird erheblich besser durch die Falzung unter den hier beschriebenen Bedingungen und die daran anschließende Messung der Bruchlast. Hier ergibt sich ein Spearman'scher Rangkorrelationskoeffizient[5] (siehe Anhang 2) von $\rho = 0{,}9132$ (Tab. 6 Zeile 9).

Damit ist die Korrelation bei den Bruchlastwerten nach Falzung auch noch besser als bei der Bestimmung der Dauerbiegezahlen ($\rho = 0{,}8807$), wobei beide Rangkorrelationskoeffizienten eine Übereinstimmung mit der Standardklassifizierung von mehr als 99,9 % statistischer Sicherheit aufzeigen. Dies bedeutet, daß sowohl die Dauerbiegezahl als auch die Bruchlast nach Falzung entsprechend dem hier beschriebenen Verfahren für die Beurteilung der Benutzbarkeit von Papier in Archiv und Bibliothek zu verwenden sind. Die Bestimmung der Dauerbiegezahl erfordert freilich einen wesentlich höheren Arbeitsaufwand als die Bestimmung der Bruchlast nach Falzung.

Beide Verfahren ergaben für die einzelnen Papiere relativ große Streuungen der Meßwerte, die Standardabweichungen aus 10 Messungen können 50 % der Meßwerte und mehr betragen. Trotzdem ergab die Berücksichtigung der Standardabweichung (Zeile 3/4 und 7/8 in Tab. 5 und 6) keine verbesserte Korrelation mit der Standardklassifizierung, so daß vorzuschlagen ist, bei der meßtechnischen Beurteilung der Benutzbarkeit gealterter Papiere auf die Berücksichtigung der Standardabweichung zu verzichten. Weiter wurde geprüft, ob die Berücksichtigung der Bruchlast vor der Falzung, etwa durch Errechnen der Verringerung der Bruchlast durch die Falzung, eine Verbesserung der Korrelation mit der Standardklassifizierung der Papiere ergibt. Dies war nicht der Fall. Die durchschnittliche Bruchlast nach einer Falzung aus einer statistisch hinreichend großen Anzahl von Prüfstreifen 15 mm x 100 mm erwies sich also als beste Grundlage für die Beurteilung der „Benutzbarkeitsqualität" gealterter Papiere in Archiv und Bibliothek.

Der Zusammenhang zwischen subjektiver Qualitätsbeurteilung auf der einen und Dauerbiegezahl bzw. Bruchlast nach Falzung auf der anderen Seite erscheint wie gesagt gesichert. Um nun für Restaurator und Bibliothekar einen Zusammenhang herzustellen zwischen den als abstrakte Zahlen vorliegenden Meßergebnissen und verbalen, mit konkreter Vorstellung erfüllten Zustandsbeschreibungen, wurde eine Zuordnung der Meßwerte bzw.

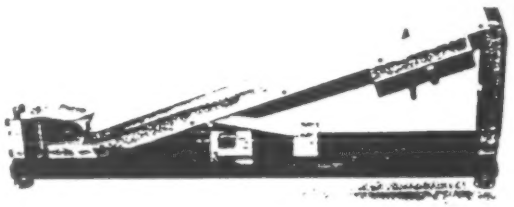

Abb. 4 Falzgerät

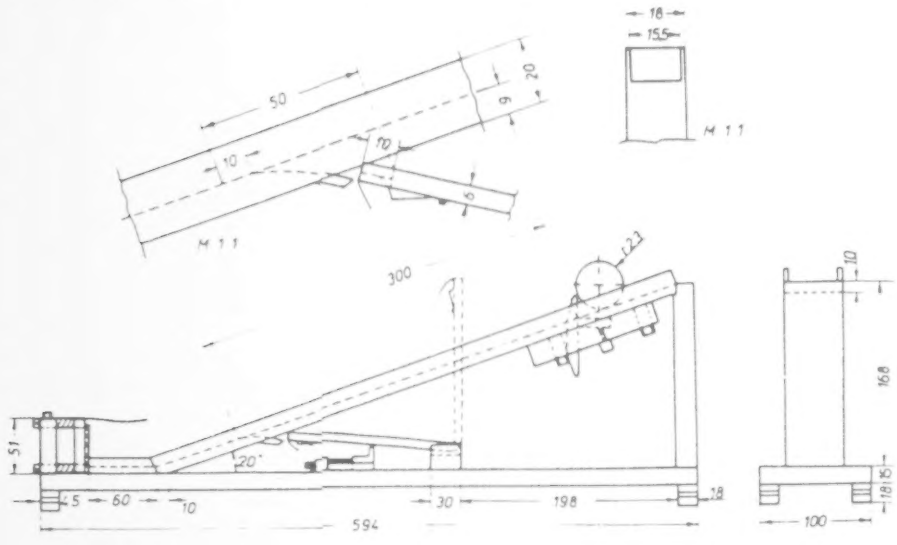

Abb. 3 Falzgerät (Konstruktion)

Tab. 5 Bruchlast

Z.	Papier Nr.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
1	F MD (N)	74,18	73,30	39,82	37,74	10,73	32,23	30,94	18,48	23,49	49,94	40,35	10,33	8,90	24,46	26,74	35,16	7,36	41,74	53,46
2	Rangzahl	1	2	7	8	16	10	11	15	14	4	6	17	18	13	12	9	19	5	3
3	F – 2s (N)	69,12	70,53	36,20	35,11	0	18,46	25,07	8,95	18,09	37,12	36,58	5,95	7,32	21,36	22,06	29,57	0,59	35,06	49,26
4	Rangzahl	2	1	6	7	19	13	10	15	14	4	5	17	16	12	11	9	18	8	3
5	F CD (N)	45,40	31,35	13,01	28,61	2,80	23,60	19,25	12,73	15,57	21,39	17,04	7,52	5,23	17,60	13,22	17,48	5,78	17,99	44,59
6	Rangzahl	1	3	14	4	19	5	7	15	12	6	11	16	18	9	13	10	17	8	2
7	F – 2s (N)	42,11	28,08	11,45	24,60	0	8,53	16,54	5,13	14,71	17,50	15,19	1,32	3,22	10,09	11,61	12,94	4,11	15,84	38,84
8	Rangzahl	1	3	12	4	19	14	6	15	9	5	8	18	17	13	11	10	16	7	2
9	Mittelwert aus Zeile 2 u. 6	1	1,5	11	5	17	7	9	15	14	4	8	16	18,5	12	13	10	18,5	6	1,5
0	Rangzahl d. Standardklassifizierung	4	3	7	2	15	1	12	14	11	8,5	8,5	18,5	18,5	17	16	13	10	6	5

Spearman'sche Rangkorrelationskoeffizienten: Zeile 0–2: $\rho = 0{,}7351$
0–4: $\rho = 0{,}6575$
0–6: $\rho = 0{,}7469$
0–8: $\rho = 0{,}6711$
0–9: $\rho = 0{,}7952$

Tab. 6 Bruchlast nach Falzung

Z.	Papier Nr.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
1	F MD (N)	66,54	67,62	28,21	37,29	5,40	33,21	19,26	15,12	18,07	34,15	28,15	0	0	1,38	6,41	11,82	7,75	36,62	30,04
2	Rangzahl	2	1	8,5	3	16	6	10	12	11	5	8,5	18,5	18,5	17	15	13	14	4	7
3	F – 2s (N)	60,38	55,19	21,32	34,34	0	21,98	10,50	13,39	8,11	29,58	21,87	0	0	0	2,89	4,51	4,58	26,76	23,93
4	Rangzahl	1	2	9	3	17,5	7,5	11	10	12	4	7,5	17,5	17,5	17,5	15	13,5	13,5	5	6
5	F CD (N)	43,22	31,97	10,83	25,67	3,66	16,19	9,30	11,10	16,03	19,67	15,85	0	0	2,44	7,11	8,20	4,91	14,61	20,83
6	Rangzahl	1	2	11	3	16	6	12	10	7	5	8	18,5	18,5	17	14	13	15	9	4
7	F – 2s (N)	39,38	29,08	9,14	23,11	0	4,74	5,59	3,18	13,30	16,80	14,19	0	0	0	2,86	6,02	2,64	11,30	12,76
8	Rangzahl	1	2	9	3	17,5	12	11	13	6	4	5	17,5	17,5	17,5	14	10	15	8	7
9	Mittelwert aus Zeile 2 u. 6	1,5	1,5	10	3	16	6	11,5	11,5	9	4	8	18,5	18,5	17	14,5	13	14,5	7	5
0	Rangzahl d. Standardklassifizierung	4	3	7	2	15	1	12	14	11	8,5	8,5	18,5	18,5	17	16	13	10	6	5

Spearman'sche Rangkorrelationskoeffizienten: Zeile 0–2: $\rho = 0{,}9276$
0–4: $\rho = 0{,}8943$
0–6: $\rho = 0{,}8803$
0–8: $\rho = 0{,}7807$
0–9: $\rho = 0{,}9132$

Tab. 7 Einstufung nach der „Benutzbarkeitsqualität" anhand der subjektiven Beurteilung, der Dauerbiegezahl und der Bruchlast nach Falzung

Klasse	Beschreibung	Standardklassifizierung: Rangziffer	Standardklassifizierung: Papiermuster	Dauerbiegezahl λ = 30°: Belastung F (N) ≙ m in (g)	Dauerbiegezahl λ = 30°: Biegezahlen n	Dauerbiegezahl λ = 30°: zutreffend für Papiermuster	Bruchlast nach Falzung: Bruchlast F (N)	Bruchlast nach Falzung: zutreffend für Papiermuster
I	sehr fest, strapazierfähig	1.– 4	1, 2, 4, 6	7,848 ≙ (800 g)	> 1000 MD + CD	1, 2, 4	> 36 MD o. CD	1, 2, 4
II	fest	5– 7	3, 18, 19	7,848 ≙ (800 g)	> 1000 MD o. CD	6	> 12 MD + CD	6, 9, 10, 11, 18, 19
III	uneingeschränkt benutzbar	8.–10	10, 11, 17	2,943 ≙ (300 g)	> 1000 MD u. CD	3, 7, 8, 9, 10, 11, 18, 19	> 12 MD o. CD	3, 7, 8
IV	benutzbar	11.–13	9, 7, 16	2,943 ≙ (300 g)	> 1000 MD o. CD	5	> 4 MD + CD	15, 16, 17
V	mit Vorsicht noch benutzbar	14.–16	8, 5, 15	0,490 ≙ (50 g)	> 1000 MD u. CD	15, 16, 17	> 4 MD o. CD	5
VI	gefährdet	17	14	0,490 ≙ (50 g)	> 1000 MD o. CD	14	noch meßbar MD und CD	14
VII	unbrauchbar	18 u. 19	12, 13	0,490 ≙ (50 g)	< 1000 MD o. CD	12, 13	nicht meßbar MD o. CD	12, 13

der Rangstufung in der Standardklassifizierung zu sinnvoll erscheinenden „Benutzbarkeitsklassen" versucht. Das Ergebnis ist in Tab. 7 festgehalten. Aus ihr geht sehr deutlich die bereits konstatierte besonders gute Übereinstimmung zwischen Bruchlastwerten nach Falzung und der Standardklassifizierung hervor. Die unübersehbaren Abweichungen lassen sich einleuchtend erklären.

1. Papier Nr. 6 und 17 sind alte, handgeschöpfte Ha-

dernpapiere, an Griff, Klang und an dem Text, den sie tragen, auf den ersten Blick als solche erkennbar, im Gegensatz zu den Hadernpapieren des 19. Jahrhunderts Nr. 5 und 18. Sie erhielten bei der Beurteilung durch Personen, die vorwiegend mit altem Papier umgehen und für die der Begriff „handgeschöpftes Hadernpapier" von vornherein einen positiven Begriff darstellt, offenbar einen „Hadernbonus", der jeweils eine Klasse ausmacht gegenüber der objektiven Qualitätsbeurteilung durch Messung der Bruchlast nach Falzung.

2. Papier Nr. 10, ein gestrichenes Papier, dürfte in negativer Analogie zu den Hadernpapieren einen „Modernitätsmalus" erhalten haben.

3. Papier Nr. 3, 7, 8, 9, 11 und 15 sind Holzschliffpapiere, Nr. 3 ein neues, Nr. 7, 8, 9, 11 und 15 mehrere Jahrzehnte alt und vergilbt. Allein der Neuzustand und die fehlende Vergilbung hat Nr. 3 offenbar eine bessere subjektive Beurteilung eingebracht als die Meßwerte rechtfertigen. Bei den übrigen Papieren hat, wie es scheint, der Vergilbungszustand die subjektive Beurteilung beeinflußt. Am auffälligsten ist dies bei Nr. 8. Hier ist der Abbau ziemlich weit fortgeschritten, das Papier ist bruchig und restaurierbedürftig – aber nur am Rand. Für diesen Rand mag die subjektive Klassifizierung „mit Vorsicht noch benutzbar" zutreffen, für das Blattinnere, aus dem die Streifen für die Messungen genommen wurden, trifft sie nicht zu. Bemerkenswert ist, daß der Qualitätsunterschied, der sich aus der unterschiedlichen Lagerung des gleichen Papiers (Nr. 8 und 9) ergibt, mit der Messung von Bruchlast nach Falzung noch erfaßt wird, ebenso wie bei der subjektiven Beurteilung, wenn auch auf anderem Niveau.

Dies letztere läßt hoffen, daß die Messung der Bruchlast nach Falzung und die Zuordnung ihrer Ergebnisse zu Benutzbarkeitsklassen ein hinreichend feines Instrument darstellt zur Zustandsbeschreibung von Bibliotheksbeständen, zur Erfassung lagerungsbedingter Qualitätsunterschiede, zur Beschreibung des Erfolgs von Restaurierungsmaßnahmen, usw. Neben der sehr guten Korrelation zur subjektiven Qualitätsbeurteilung bietet sie den Vorteil, daß ihre Werte rasch und ohne großen Aufwand zur Verfügung stehen. Eine statistisch hinreichend große Anzahl (je 10 in beiden Richtungen längs und quer) von Probestreifen von 15 mm Breite und 100 mm Länge wird vorgefalzt. Dann wird die Bruchlast gemessen. Bei der Beurteilung der „Benutzbarkeitsqualität" wird folgendermaßen eingestuft:

Klasse I sehr fest, strapazierfähig	$F > 36$ N in einer oder in beiden Richtungen
Klasse II fest	$36\ N > F > 12$ N in beiden Richtungen
Klasse III voll benutzbar	$36\ N > F > 12$ N in einer der beiden Richt
Klasse IV benutzbar	$12\ N > F > 4$ N in beiden Richtungen
Klasse V (mit Vorsicht) noch benutzbar	$12\ N > F > 4$ N in einer der beiden Richt
Klasse VI gefährdet	Bruchlast nach Falzung in beiden Richtungen noch meßbar
Klasse VII nicht mehr benutzbar	Bruchlast nach Falzung nicht mehr meßbar

Es läge in der Analogie der hier vorgeschlagenen Klassifizierung, die Skala nach oben und unten um je eine Stufe zu erweitern:

Klasse 0	$F > 36$ N in beiden Richtungen
Klasse I	$F > 36$ N in einer der beiden Richtungen
Klasse VII	Bruchlast nach Falzung in einer der beiden Richtungen noch meßbar
Klasse VIII	Bruchlast nach Falzung in keiner Richtung mehr meßbar

Für Klasse 0 liegt im Bereich von Bibliothek und Archiv kein Bedürfnis vor, Klasse VIII (bzw. Klasse VII, wenn Klasse VIII herangezogen werden soll) ist unter den 19 Proben, die die Grundlage dieser Arbeit bilden, nicht vertreten.

Es bleibt abzuwarten, ob die Forschung zur Restaurierungskunde diese hier vorgeschlagene Messung und Beurteilung akzeptiert und ob sie sich in der Zukunft bewährt.

Anhang 1:

Berechnung des Kendall'schen Übereinstimmungskoeffizienten W (5,6)

$$W = \frac{12 \sum_{i=1}^{N} (\xi_i - \bar{\xi})^2}{K^2 \times N \, (N^2 - 1)}$$

$$\bar{\xi} = 1/2 \, (N + 1) \, K$$

für $N > 7$ berechnet sich die Prüfgröße P zu

$$P = K \, (N - 1) \, W$$

ξ_i = Summe der einer Probe durch die verschiedenen Beobachter zugeteilten Rangziffern

K = Zahl der Beobachter

N = Zahl der Proben

W nähert sich für volle Übereinstimmung dem Wert 1,000.

Zur Angabe der statistischen Sicherheit ist P zu vergleichen mit den Werten von χ^2 für $n = N - 1$.

Die χ^2-Werte sind für N = 19 (n = 18) bei den angegebenen statistischen Sicherheiten S:

$S = 95\ \% \rightarrow \chi^2 = 28{,}869$

$S = 99\ \% \rightarrow \chi^2 = 34{,}805$

$S = 99{,}9\ \% \rightarrow \chi^2 = 42{,}312$

Anhang 2:

Berechnung des Rangkorrelationskoeffizienten ρ nach Spearman (5)

$$\rho = 1 - 6 = \frac{\sum_{i=1}^{N} (u_i - v_i)^2}{N \, (N^2 - 1)}$$

u_i, v_i: Rangziffern der Beurteilung des Produkts
u – durch den ersten Beobachter
v – durch den zweiten Beobachter

N: Zahl der Proben

ρ nähert sich für volle Übereinstimmung der Beurteilung der zwei Beobachter dem Wert + 1,00

Für N = 19 (unser Beispiel) errechnet sich die Prüfgröße P zu:

$$P = \frac{\sqrt{N-2}}{1-\rho^2}$$

Zur Angabe der statistischen Sicherheit ist P zu vergleichen mit den Integralgrenzen der t-Verteilung für den Freiheitsgrad n = N – 2. Die Integralgrenzen liegen in unserem Beispiel bei den statistischen Sicherheiten S bei folgenden Werten

S = 95 % → t = 2,11
S = 99 % → t = 2,90
S = 99,9 % → t = 3,96

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Österreich

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SECTION VI

ACCELERATED AGING

VI. ACCELERATED AGING

The best way of measuring the stability of strength properties over time is by natural aging. But, real-time studies are an impractical method for assessing the long-term use of paper. Techniques of chemical kinetics, on the other hand, provide a means of effectively accelerating the natural aging process. There are TAPPI methods for simulating two different aging environments. Method T-453 describes a method for evaluating the effect of dry heat on paper properties, while Method T-544 is used for evaluating the effect of moist heat on the properties of paper.

It is known that moisture greatly accelerates the aging of paper. In fact, an increase in moisture content leads to a strong acceleration of the aging of paper. In order to be representative of natural conditions in many countries where conditions of high humidity, and perhaps high temperature, are common, it is desirable that in an accelerated aging atmosphere the paper should have the same moisture content as in a natural aging atmosphere. In general, this applies to properties such as fold number and brightness. Therefore, dry-heat aging of paper is less sensitive. However, dry-heat aging is considerably easier to accomplish. The moist-heat method utilizes a laboratory apparatus to maintain an environment of 90°C and a relative humidity of 50% while the dry method uses a mechanically convected oven to maintain the temperature at 105°C.

For comparing various treatments of paper, dry aging is a convenient screening, and the ovens are considerably less expensive than humid aging ovens. Furthermore, humid aging ovens should be fed with distilled or deionized water because of the chlorine in most city waters, the ovens must be drained and cleaned between each test run to avoid cross-contamination by impurities building up in the water pans of the ovens.

Aging studies are carried out using TAPPI Method T-544 at 90°C and 50% RH by vertical suspension of 2" wide strips of paper in a mechanically convected oven (the oven is to maintain the temperature within $\pm$ 0.5°C and the humidity within 1%). The samples must be kept separated due to the possibility of volatile acids migrating between test strips, leading to erroneous results. Samples are removed at seven day intervals for a total of 35 days.

T 453 om-89

TENTATIVE STANDARD – 1941
OFFICIAL STANDARD – 1948
SUGGESTED METHOD – 1970
PROVISIONAL METHOD – 1985
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Effect of dry heat on properties of paper

1. Scope

1.1 This method specifies the procedure for dry heat treatment of paper or board and the general procedure for testing the heat-treated materials. The purpose is to obtain, by an accelerated test, inferences regarding the aging qualities of the paper.

1.2 The effect of moist heat on the strength of paper may be determined by T 544 "Effect of Moist Heat on Properties of Paper and Board." It has been determined that the degradation of cellulose is very sensitive to moisture (*1,2*). Comparison of accelerated aging with natural aging indicates that some moisture should be present in an accelerated aging atmosphere (*3*). Dry heat aging of cellulose is much less sensitive and probably does not rank papers in order of suitability as accurately as moist heat aging. It is much simpler to use and may be adequate for many purposes, but moist heat aging should be considered where the greatest correlation with natural aging is needed (*6, 7*).

1.3 The procedure is considered suitable for estimating the relative stability of chemical wood papers and cotton content papers. It has not been established that this method is suitable for papers containing groundwood.

1.4 No evidence is available that it is reliable for coated papers or for those containing wet-strength resins.

2. Significance

2.1 It is assumed that the heating conditions specified in this method cause deteriorative reactions which, excepting color changes, approximate those occurring to the normal components of paper on long aging of the paper in air at room temperature.

2.2 It is recognized that heating paper under the conditions specified is not a normal treatment which the paper would receive in use (*4*). The purpose, however, is to obtain, by an accelerated test, information regarding the relative aging qualities of paper. Research has suggested that, except for color changes, the results of heating under the prescribed conditions generally correlate with those of normal aging.

2.3 Properties compared before and after such exposure include mechanical properties, such as folding endurance and tearing resistance, and chemical properties, such as pH and alkali resistance. The test used in prior versions of this method was folding endurance.

3. Apparatus

3.1 *Oven*, forced ventilation, that will maintain a uniform temperature of 105° ± 2°C where the specimens are located, with means of shielding them from direct radiation from the heating elements (ASTM E 145, Type II, Grade A).

NOTE 1: This is a closer temperature control than the usual ±3°C. It also refers to the actual temperature surrounding the specimen.

4. Test methods

4.1 One or more of the following TAPPI methods may be used for estimating the effect of dry heat treatment of papers:

4.1.1 TAPPI T 509 "Hydrogen Ion Concentration (pH) of Paper Extracts (Cold Extraction Method)."

4.1.2 TAPPI T 511 "Folding Endurance of Paper (MIT Tester)."

4.1.3 TAPPI T 423 "Folding Endurance of Paper (Schopper Type Tester)."

4.1.4 TAPPI T 494 "Tensile Breaking Properties of Paper and Paperboard (Using Constant Rate of Elongation Apparatus)."

4.1.5 TAPPI T 456 "Wet Tensile Breaking Strength of Paper and Paperboard."

4.1.6 TAPPI T 430 "Copper Number of Pulp, Paper, and Paperboard."

Approved by the Physical Properties Committee of the Process and Product Quality Division TAPPI

4.1.7 TAPPI T 412 "Moisture in Paper and Paperboard." Moisture regain may be calculated from data obtained by this procedure.

4.1.8 TAPPI T 212 "One Percent Sodium Hydroxide Solubility of Wood and Pulp."

4.2 *Zero-span tensile strength:* Although there is a TAPPI procedure for zero span breaking length of pulp (TAPPI T 231 "Zero-Span Breaking Length of Pulp"), there is none for paper. Commercial instruments are available for measuring the zero-span tensile strength of paper.

4.3 Folding endurance is the *preferred test* for estimating the effect of dry heat treatment on paper. A *pH value should always be determined* for all aging periods.

5. Sampling

Obtain a sample of the paper in accordance with T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Product," obtaining enough paper to provide for specimens as required for Section 6, with a minimum of 5 sheets for each test for each control and for each level of heat exposure.

6. Test Specimens

6.1 For T 423 or T 511 cut each control specimen and the corresponding specimen to be heated, in the machine direction in line with, and contiguous to, each other in accordance with the directions in the relevant TAPPI method. For these methods a minimum of 10 specimens is required for each control and exposure.

6.2 For the other TAPPI methods listed in section 4 specimens should be prepared in accordance with the appropriate section of the relevant method.

7. Procedure

7.1 Precondition the control specimens only, by placing them in a desiccator at room temperature over calcium chloride for 2 h or longer.

7.2 Suspend the other specimens to be heated in the oven so that the air of the oven has free access to all surfaces of each strip and so that the strips do not touch any part of the oven. Heat at 105° ± 2°C for 24 ± 0.25 h, 48 ± 0.5 h, 72 ± 0.75 h, and 144 ± 1.5 h. Keep the oven closed and ensure that no other material is in the oven during the heat treatment.

NOTE 2: The ambient air around a recirculating oven can affect the RH in the oven. Ideally, the oven should be maintained in a room at 23°C and 50% RH. If the oven is not located in a controlled environment, the RH of the ambient air should be reported.

7.3 After oven aging, condition the desiccataed and the heated specimens side by side for 24 h in an atmosphere in accordance with T 402 "Standard Conditioning and Testing Atmospheres for Paper, Board, Pulp Handsheets, and Related Products," and then test them as described in the relevant TAPPI method.

8. Treatment of data

8.1 The following are some of the ways that the data may be presented.

8.1.1 Plot the data, or the log of the data, as a function of time and calculate the slope. The slopes of various papers can then be compared.

8.1.2 Based on the control value as 100%, calculate the percent of the property retained. Retentions may also be plotted. Retentions of log folding endurance, pH, and air permeability are not applicable.

8.1.3 From a plot of degradation as a function of time, calculate the half-life of the paper.

8.2 A test for statistical significance of change in properties due to accelerated aging should be made.

9. Report

9.1 Include the following particulars in the test report: reference to this TAPPI method and reference to the TAPPI method, if any, or another method to which the testing procedure conformed.

9.2 Include also in the test report, as specified by the method to which the testing procedure conformed, the following particulars:

9.2.1 Complete identification of the sample.

9.2.2 Date and place of testing.

9.2.3 The time, temperature, and relative humidity of testing.

9.2.4 The mean value and precision of the measured value of the appropriate property of the untreated material.

9.2.5 The mean value and precision of the measured value of the appropriate property of the treated material.

9.2.6 Any other treatment of data agreed upon between vendor and purchaser.

9.2.7 Any deviations from the relevant TAPPI methods or other methods used or any circumstances or influences which might have affected the test results.

10. Precision

10.1 The precision of the individual test method will be found in the relevant TAPPI method.

10.2 The effect of the heat treatment on the precision of the individual test methods is unknown.

11. Statistical significance

11.1 In order to compare the performance of two materials (in this case, unaged and aged paper), it is assumed that the variability in performance of each (A, unaged, and B, aged) is unknown but can be assumed to be about the same (*5*).

After the arithmetic means (x_A) and (x_B) and the standard deviations of test results (s_A and s_B) are calculated, a pooled value s_p, for the standard deviation is calculated:

$$s_p = \frac{(n_A - 1)s_A^2 + (n_B - 1)s_B^2}{n_A + n_B - 2}$$

where n_A = number of test specimens of unaged papers, and n_B = number of test specimens of aged papers.

11.2 Then a value for u, the test criterion for detecting a difference at 95% confidence, may be calculated:

$$u = t\, s_p \frac{n_A + n_B}{n_A n_B}$$

11.3 The value of t is obtained from a statistical table of t distribution and depends on the number of observations and the specified confidence level.

11.4 If $x_A - x_B$ is larger than u, one can conclude that there is a true difference, with 95% confidence of being right, between the performances of A and B. This procedure may be used if $n_A = n_B$.

12. Additional Information

12.1 Effective date of issue: July 1, 1989.

12.2 Information for predicting the comparative stability of paper appearing in the literature (*6,7*) indicates that moist aging may be much superior to dry aging.

12.3 Since it is not possible to describe a normal environment, it is not possible to relate accelerated aging to normal aging. This method and the related moist heat method may be used in establishing ranking orders of several papers. Knowledge of the environment in which papers are expected to be used or stored might aid in the selection of the dry heat or moist heat test methods. For further information regarding the relationship between test methods and normal aging, see the reports noted in the references (*8-14*).

12.4 Related method:

(a) ASTM D 776 (procedure technically identical).
(b) ISO 5630/1 Paper and Board Accelerated Aging
(c) TAPPI T544 Effect of Moist Heat on Properties of Paper and Board

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Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Test Methods Administrator. ■

T 544 pm-85
PROVISIONAL METHOD—1985
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Effect of moist heat on properties of paper and board

1. Scope

1.1 This method specifies the procedure for humidified heat treatment of paper or board and the general procedure for testing the heat-treated materials. The purpose is to obtain, by an accelerated test, inferences regarding the aging qualities of the paper.

1.2 The method is based on work done on printing and writing papers but may be used with discretion for other types of papers and boards. The procedure is not applicable to certain electrical insulating papers, for which different conditions apply.

2. Summary

Properties of paper or board are compared before and after "accelerated aging" in a humidified atmosphere at an elevated temperature.

3. Significance

3.1 Exposure of paper or board to a hostile environment, such as some types of radiation, elevated temperature, or chemical attack over a period of hours, may provide information concerning the natural changes that may occur in the material over a period of years.

3.2 Hostile environments that have been used include exposure to heat, to heat and moisture, to visible and ultraviolet radiation, and to sulfur dioxide gas.

3.3 Properties compared before and after such exposure include mechanical properties, such as folding endurance and tearing resistance, optical properties, such as brightness and opacity, and chemical properties, such as pH and alkali resistance.

3.4 TAPPI T 453 "Effect of Dry Heat on Properties of Paper" is available for determining the effect of dry oven treatment on paper. It has been determined that the degradation of cellulose is very sensitive to moisture (*1, 2*). Comparison of accelerated aging with natural aging indicates that some moisture should be present in an accelerated aging atmosphere (*3*). Dry accelerated aging of cellulose is much less sensitive and probably does not rank papers in order of stability as accurately as moist accelerated aging. Dry aging is much simpler to use and may be adequate for many purposes, but moist accelerated aging should be used where the greatest correlation with natural aging is needed.

4. Apparatus

4.1 *Apparatus for maintaining a temperature of 90°C and 25% relative humidity* is required (Fig. 1). Graminski (*1, 2*) has shown that the rate of degradation of folding endurance and of zero span tensile can be approximately doubled by raising the relative humidity at 90°C from 20% to 30%. Therefore, the temperature must be controlled to less than 0.5°C (preferably 0.1°C) in order to hold the relative humidity variation within 1%.

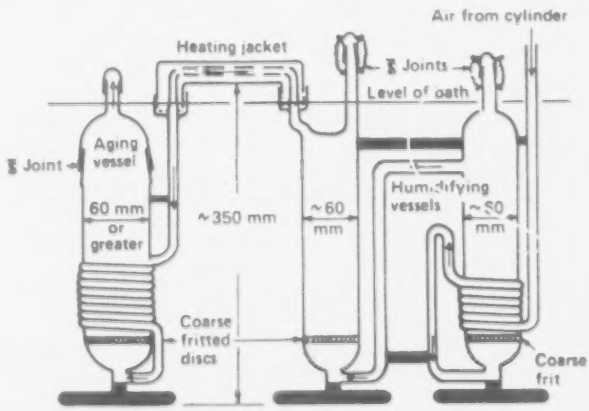

Fig. 1. Apparatus for maintaining temperature of 90°C and 25% RH

4.1.1 A very precise procedure for maintaining the required temperature and relative humidity is by the use of constant temperature baths. Two baths are required.

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In the first bath, which is maintained at 57.3°C (the vapor pressure of water at 57.3°C is one-fourth of the vapor pressure at 90°C), purified air from a cylinder is saturated with water vapor in tandem frittered glass bubblers. This air is led through a heated (to prevent condensation) glass or stable plastic tube to an aging vessel in a bath held at 90 ± 0.1°C. The air should be passed through a coil of glass tubing in the bath held at 90°C, preferably wrapped around the aging vessel, in order to ensure that the air has reached 90°C before it enters the aging vessel.

4.1.2 Humidifier vessels about 60 mm in diameter and 250 mm high have been found to be satisfactory. Aging vessels about 60 mm in diameter and 300 mm high, including a 60/50 standard taper joint, are suitable for the purpose, but other sizes may be used.

4.2 *Test instruments*, depending on the test, or tests, selected for evaluation.

5. Test methods

5.1 One or more of the following TAPPI methods may be used for estimating the effect of moist heat treatment on paper:

5.1.1 TAPPI T 509 "Hydrogen Ion Concentration (pH) of Paper Extracts (Cold Extraction Method)."

5.1.2 TAPPI T 511 "Folding Endurance of Paper (MIT Tester)."

5.1.3 TAPPI T 423 "Folding Endurance of Paper (Schopper Type Tester)."

5.1.4 TAPPI T 494 "Tensile Breaking Properties of Paper and Paperboard (Using Constant Rate of Elongation Apparatus)."

5.1.5 TAPPI T 456 "Wet Tensile Breaking Strength of Paper and Paperboard."

5.1.6 TAPPI T 430 "Copper Number of Pulp, Paper, and Paperboard."

5.1.7 TAPPI T 412 "Moisture in Paper and Paperboard." Moisture regain may be calculated from data obtained by this procedure.

5.1.8 TAPPI T 212 "One Percent Sodium Hydroxide Solubility of Wood and Pulp."

5.1.9 TAPPI T 452 "Brightness of Pulp, Paper, and Paperboard (Directional Reflectance at 457 nm)."

5.2 *Zero-span tensile strength*: Although there is a TAPPI procedure for zero span breaking length of pulp (TAPPI T 231 "Zero-Span Breaking Length of Pulp"), there is none for paper. Commercial instruments are available for measuring the zero-span tensile strength of paper.

5.3 Folding endurance is the *preferred test* for estimating the effect of moist heat treatment on paper. A *pH value should always be determined* for all aging periods.

6. Sampling

Select a sample of paper according to TAPPI T 400 "Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, or Related Product" and using any special directions given in the test method(s) used for evaluation.

7. Test specimens

7.1 Select at random and prepare five sets of test specimens in accordance with the TAPPI method(s) relevant to the required test(s).

7.2 Protect the test specimens from strong light.

7.3 Avoid as much as possible handling with the bare hands, and avoid undue exposure to the atmosphere of a chemical laboratory.

8. Procedure for heat treatment

8.1 Suspend four of the five sets of test specimens in aging vessels in the constant temperature bath. Pass air at the rate of 50 ± 25 mL/min at 90°C and 25% relative humidity through the aging vessels in the constant temperature bath. The rate of flow of air is not critical.

8.2 Remove a set of test specimens at 24 ± 0.25 h, 48 ± 0.5 h, 72 ± 0.75 h, and 144 ± 1.5 h. Longer aging times may be used, if necessary, but more test specimens will be needed.

NOTE 1: By agreement between vendor and purchaser, all of these specified times may be used and the data plotted, or the data from only one time taken and compared with the control.

NOTE 2: The reaction vessel should not contain more than one type of paper at any time, in order to prevent the possibility of contamination by distillation or sublimation of products.

9. Conditioning

9.1 At least 2 h, and preferably overnight, before completion of the heat treatment, place the untreated set of test specimens in a desiccator or other preconditioner maintained at 10–35% relative humidity at 23°C.

9.2 On completion of the heat treatment, transfer both the treated and untreated sets of test specimens to the same conditioned enclosure as described in TAPPI T 402 "Standard Conditioning and Testing Atmospheres for Paper, Board, Pulp Handsheets, and Related Products."

10. Procedure for testing

Test each set of test pieces as described in the relevant TAPPI method or by another appropriate method.

11. Treatment of data

11.1 The following are some of the ways that the data may be presented:

11.1.1 Plot the data, or the log of the data, as a function of time and calculate the slope. The slopes of various papers can then be compared.

11.1.2 Based on the control value as 100%, calculate the retention, percent, of the property. Retentions may also be plotted. Retentions of log folding endurance, pH, and air permeability are not applicable.

11.1.3 From a plot of degradation as a function of time, calculate the half-life of the paper.

11.1.4 A test for statistical significance of change in properties due to accelerated aging should be made.

12. Report

12.1 Include the following particulars in the test report: reference to this TAPPI method and reference to the TAPPI method, if any, or another method to which the testing procedure conformed.

12.2 Include also in the test report, as specified by the method to which the testing procedure conformed, the following particulars:

12.2.1 Complete identification of the sample.

12.2.2 Date and place of testing.

12.2.3 The time, temperature, and relative humidity of testing.

12.2.4 The mean value and precision of the measured value of the appropriate property of the untreated material.

12.2.5 The mean value and precision of the measured value of the appropriate property of the treated material.

12.2.6 Any other treatment of data agreed upon between vendor and purchaser.

12.2.7 Any deviations from the relevant TAPPI methods or other methods used or any circumstances or influences which might have affected the test results.

13. Precision

13.1 The precision of the individual test method will be found in the relevant TAPPI method.

13.2 The effect of the heat treatment on the precision of the individual test methods is unknown.

14. Statistical significance

14.1 In order to compare the performance of two materials (in this case, unaged and aged paper), it is assumed that the variability in performance of each (A, unaged, and B, aged) is unknown but can be assumed to be about the same (*4*). After the arithmetic means ($\bar{x}_A$ and $\bar{x}_B$) and the standard deviations of test results (s_A and s_B) are calculated, a pooled value, s_p, for the standard deviation is calculated:

$$s_p = \frac{(n_A - 1)s_A^2 + (n_B - 1)s_B^2}{n_A + n_B - 2}$$

where n_A = number of test specimens of unaged papers, and n_B = number of test specimens of aged papers.

14.2 Then a value for u, the test criterion for detecting a difference at 95% confidence, may be calculated:

$$u = t\, s_p \frac{n_A + n_B}{n_A n_B}$$

14.3 The value of t is obtained from a statistical table of t distribution and depends on the number of observations and the specified confidence level.

14.4 If $\bar{x}_A - \bar{x}_B$ is larger than u, one can conclude that there is a true difference, with 95% confidence of being right, between the performances of A and B. This procedure may be used if $n_A = n_B$.

15. Additional information

15.1 Effective date of issue: October 1, 1984.

15.2 This method is practically identical to proposed ISO method "Paper and Board — Moist Heat Treatment (Accelerated Aging)" (ISO DP 5630/2, 6 N 579).

References

1. Graminski, E.L., Parks, E.J., and Toth, E.E., "The Effects of Temperature and Moisture on the Accelerated Aging of Paper," ACS Symposium Series No. 95, *Durability of Macromolecular Materials*, R.K. Eby, Editor.
2. Graminski, E.L., Parks, E.J., and Toth, E.E., "The Effects of Temperature and Moisture on the Accelerated Aging of Paper," NBSIR 78-1443, Report to the National Archives and Records Service; available from National Technical Information Services (NTIS), Springfield, VA 22151.
3. Wilson, W.K., and Parks, E.J., "Comparison of Accelerated Aging of Book Papers in 1937 with 36 Years Natural Aging," *Restaurator* **4**: 1 (1980).
4. Natrella, Mary Gibbons, NBS Handbook No. 91, Experimental Statistics, 1966.

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Test Methods Administrator. ■

SECTION VII

CHEMICAL EFFECTS POST ACCELERATED AGING

VII. CHEMICAL MEASUREMENTS

Treated and untreated paper which has been subjected to accelerated aging are evaluated with respect to their chemical properties. This allows one to gain insight into the level of permanency of the process under evaluation. The procedures to be employed on paper subjected to accelerated aging are described in detail in Section IV.

SECTION VIII

PHYSICAL EFFECTS POST ACCELERATED AGING

VIII. PHYSICAL MEASUREMENTS

Untreated and treated paper which has been subjected to accelerated aging are evaluated with respect to their physical properties as described in Section V. The measurements are important indicators in the enhancement of life of the treated articles.

SECTION IX

NON-DETRIMENTAL EFFECTS

IX. NON DETRIMENTAL EFFECTS

EMPIRICAL CONDITIONS

This area represents the realm of most discussions of treatment processes. Knowledge of book components and conservation practices allows conservators in place to critique a process based upon its operating parameters. Therefore, a description of the process allows them to determine if any step will have a potential for negative impact on book components. Likewise, they are able to determine if the chemistry of a particular process will give rise to deleterious effects in the treated materials. In fact, this is essentially the extent of most evaluations performed to date. While process parameters may give rise to caution, what is essentially done here is an empirical test. The treated materials are compared to untreated ones by looking, feeling and comparing. This test is extremely useful to assure that no damage has befallen the components of a book upon treatment, however, they are not useful for evaluating positive enhancement transferred to the books.

The visual evidence generally consists of the following:

...Little or no markings on or changes in book covers
...Little or no cockling of text block
...Little or no distortion of covers
...No change in the flexibility of bindings

Another aspect of empirical evaluations is the determination of residual odors, which is best accomplished by a comparison of aromas of untreated versus treated material and noting any, and the extent of, differences.

CHEMICAL CONDITIONS

A knowledge of the processing chemistry and familiarity with the nature of book components allows a heightened awareness of the compatibility of a treatment process with materials likely to be encountered.

The process should essentially produce a product which is indistinquishable from its pre-treated form. Chemical interactions that may affect inks, dyes, and colors of the paper should be determined, such as the use of polar solvents. Additionally, the potential for damage to other book components should be assessed.

The processing chemistry disclosure also allows for an evaluation of the safety and toxicity potential of chemicals remaining in the books. Therefore, the nature of the chemicals and/or solvents employed should be known.

PHYSICAL CONDITIONS

The requirements of a mass deacidification process should not expose the materials being treated to conditions that would endanger their integrity. Physical processing parameters which have a potential for adverse effects include the extent and duration of exposure to elevated temperatures and the level of dryness required for processing.

Also, the materials handling aspect of book and document handling should be evaluated to insure adequate protection of the books from trucking and handling operators.